VOL. VII 1905

TRANSACTIONS

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TRANSACTIONS

OF THE

AMERICAN ELECTROCHEMICAL SOCIETY

157526

VOLUME VII

SEVENTH GENERAL MEETING

BOSTON, MASS., AND CAMBRIDGE, MASS., APRIL 25, 26 AND 27, 1905

PUBLISHED BY
THE AMERICAN ELECTROCHEMICAL SOCIETY
39 SOUTH TENTH STREET, PHILADELPHIA, PA.
1905

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VOLUME VII 1905

TRANSACTIONS

OF THE

AMERICAN ELECTROCHEMICAL SOCIETY

PROCEEDINGS

MINUTES OF THE SEVENTH GENERAL MEETING OF THE SOCIETY, HELD AT BOSTON AND CAMBRIDGE, MASS., APRIL 25, 26 AND 27, 1905.

(Number of members registered, 53; guests, 16; total, 69.)

SESSION OF APRIL 25TH.

The meeting was called to order at 9.30 A. M. in the Lowell Hall of the Massachusetts Institute of Technology, President Carhart being in the chair.

Due to the number of papers on the programme, the Chairman dispensed with formalities and proceeded at once with the programme as outlined.

The following papers were then read and discussed, as printed in full in the Transactions:

"Reversible and Irreversible Polarization," by Prof. W. S. Franklin and L. A. Freudenberger.

"The Aluminum Electrolytic Condenser" (II), by C. I. Zimmerman.

"Notes on Economic Temperatures of Copper Refining Solutions," by Prof. C. F. Burgess (read by Dr. M. deK. Thompson, Jr.).

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"A Diaphragm Cell for the Electrolysis of Brine," by C. P. Townsend.

"Conduction in Electrolytes," by Dr. J. W. Richards.

"Billitzer's Method of Determining Absolute Potentials," by Prof. H. M. Goodwin.

"The Edison Storage Battery," by Dr. M. deK. Thompson, Jr.

After announcements by President Carhart and Dr. H. P. Talbot, Secretary of the Local Committee, relative to luncheon and the afternoon excursion to the works of the Thompson-Houston Electrical Co., at Lynn, the session was adjourned.

The members of the Society were received by President Pritchett, of the Institute, and entertained for luncheon at the Technology Club.

Session of April 26th.

The meeting was called to order at 9.30 A. M. at the Pierce Hall of Engineering, Harvard University.

The reports of the Treasurer, Secretary and of the standing committees were read, as presented to and accepted by the Board, as follows:

TREASURER'S ANNUAL REPORT

YEAR ENDING DECEMBER 31, 1904.

PHILADELPHIA, April 22, 1905.

To the Board of Directors of the American Electrochemical Society.

GENTLEMEN:—In accordance with the recommendation made in my last Annual Report in regard to the Secretary keeping the accounts of the Society, which recommendation was subsequently adopted by the Board, I beg to report that on May 1, 1904, all the books of accounts, bank and check books and cash balance of $3,885.59 were turned over to the Secretary, whose report will give you in detail full information in relation to the financial condition of the Society.

Cash balance December 31, 1903	$1,275.52	
Total receipts January 1, 1904, to December 31, 1904	4,695.79	
		$5,971.31
Total expenditures January 1, 1904, to December 31, 1904		4,252.25
Balance December 31, 1904		$1,719.06

Very truly yours,

PEDRO G. SALOM,

Treasurer.

SECRETARY'S ANNUAL REPORT

FROM APRIL 7, 1904, TO APRIL 25, 1905.

To the Board of Directors of the American Electrochemical Society.

GENTLEMEN:—I submit herewith the following report on the condition of the Society:

Since the last annual report the Society has held two meetings, and the transactions have been published in Volumes V and VI.

One thousand copies of each volume, bound in cloth, and 500 of each, bound in paper, were printed.

Two hundred and sixty-seven copies of Volume V and of Volume VI have been distributed to members of the Faraday Society, in accordance with the arrangement for free exchange of Transactions.

There were on hand December 31, 1904:

378	copies	Vol. I	cloth.
392	"	Vol. II	"
279	"	Vol. III	"
293	"	Vol. IV	"
240	"	Vol. IV	paper.
282	"	Vol. V	cloth.
230	"	Vol. V	paper.

And on April 20, 1905, there were on hand

362	copies	Vol. I	cloth.
379	"	Vol. II	"
264	"	Vol. III	"
276	"	Vol. IV	"

240	copies	Vol.	IV	paper.
249	"	Vol.	V	cloth.
228	"	Vol.	V	paper.
269	"	Vol.	VI	cloth.
233	"	Vol.	VI	paper.

The following data shows the condition of the Society in regard to membership:

Total number of members in April, 1904 661
Number of applicants passed upon since the last annual meeting 60
Number of resignations during the year 28
Number of deaths 4

It will be noticed, as might have been expected, that during the last year the number of applications has fallen off. It would have been practically impossible to have kept up the same rate of accessions as had taken place during the first and second years of the existence of the Society.

It is a fact, however, that the members coming in at this time are more closely identified with electrochemical interests than many who had joined at first, and the growth, although small, is a healthy one.

The chief element which will contribute to strengthening the position of the American Electrochemical Society in the future will be the character of the papers presented at its meetings, and subsequent publication. It is therefore hoped that the members will be loyal to the Society in contributing the results of their researches and industrial accomplishments, believing it will be to our mutual advantage.

It has been noticed recently by the Secretary that the Transactions have been in active demand by libraries, which shows our publication is accepted on its merits.

Balance Sheet—December 31, 1904.

ABSTRACT OF TRIAL BALANCE			INVEN'Y	LOSS	GAIN	ASSETS	LIAB'S	PROFIT AND LOSS ACCT.	
Cash	$1723.95	. . .	. . .	. . .	. . .	$1723.95			
Profit and Loss	. . .	$1452.52	. . .	. . .	. . .	. . .	. . .	. . .	$1452.52
Annual Dues	. . .	3600.00	. . .	. . .	$3600.00				
Initiation Fees	. . .	550.00	. . .	. . .	550.00				
Advertising	. . .	271.26	. . .	. . .	271.26				
Publication Account	929.99	. . .	$2370.08	. . .	1440.09	2370.08			
Expense "	1933 57	. . .	. . .	$1933.57					
Investment "	1000.00	. . .	. . .	. . .	. . .	1000.00			
Interest "	. . .	21.61	. . .	. . .	21.61				
Office Furniture	53.00	. . .	. . .	. . .	. . .	53 00			
A. B. Frenzel Prize	. . .	250.00	. . .	. . .	. . .	. . .	$250.00		
Dues from Members	820.61	. . .	. . .	. . .	. . .	820.61			
Dues Prepaid by Members	. . .	315.73	. . .	. . .	. . .	. . .	315.73		
	$6461.12	$6461.12		$1933.57	$5882.96				
BALANCE—GAIN				3949.39	. . .	. . .	. . .	. . .	$3949.39
				$5882.96	$5882.96				
						$5967.64	$565.73		
BALANCE—PRESENT PROFIT AND LOSS ACCOUNT							5401.91		$5401.91
						$5967.64	$5967.64		

Financial Statement—*Condensed Balance Sheet.*

RECEIPTS.

Cash balance, December 31, 1903	$1,275.52
From publications	388.21
From advertising	271.26
From initiation fees, 110 members at $5	550.00
From dues, 694 members at $5	3,479.12
From interest	21.61
	$5,975.72

EXPENDITURES.

Investment	$1,000.00
For publication	1,318.20
For expense	1,933.57
Balance in bank December 31, 1904, incl. $4.89 in petty cash	1,723.95
	$5,975.72

From the $1,719.06 in bank on December 31, 1904, should be deducted $584.59, the cost of printing Volume VI, and paid in 1905, leaving $1,134.47 as the net balance. To compare with previous years, the value of the bond should be added, making $2,134.47.

I also append statement of financial condition of the Society to March 31, 1905.

RECEIPTS.

Cash balance December 31, 1904	$1,723.95
From members	2,215.00
From advertisements	49.60
From publications	117.00
From coupon	17.50
	$4,123.05

EXPENDITURES.

For publications	$15.39
For expenses	489.99
Balance in bank, March 31, 1905	3,617.05
	$4,123.05

Cash in bank March 31, 1905	$3,617.67
Cash due from members	1,015.00
	$4,632.67

Examined and approved, Philadelphia, April 22, 1905.

HENRY G. MORRIS,
C. J. REED,
Auditors.

In stating more fully the financial condition of the Society for the first few months in 1905, it would be well for me to say that the Board has authorized the Treasurer and Secretary to purchase another $1,000 bond, as nearly as possible bearing 4 per cent. interest. It may be impossible for the Society to save this amount in 1905, but it was believed best to get the higher rate of interest throughout the most of the year, even if the bond might have to be realized upon towards the latter part of the current year.

S. S. SADTLER,
Secretary.

REPORT OF COMMITTEE ON PUBLICATION.

The Committee on Publication begs to report that two volumes of the Transactions, namely, Vols. V and VI, have been published since the last annual meeting. Vol. V contained the papers read

at the Annual Meeting of the Society held in Washington, D. C., April 7, 8 and 9, 1904, and three papers read at a meeting of the New York Section held January 26, 1904.

Volume VI contains the papers read at the Sixth General Meeting of the Society, held at St. Louis, September 13, 15 and 16, 1904, and one paper read at a meeting of the Philadelphia Section, December 5, 1904, and, in addition to these, the papers read in joint sessions of the American Electrochemical Society and the Fifth International Electrical Congress.

S. S. SADTLER,
Secretary.

REPORT OF COMMITTEE ON PAPERS.

The Committee on Papers would report that 44 papers have been printed in the Transactions in 1904, as compared with 45 in 1903 and 42 in 1902.

S. S. SADTLER,
Secretary.

It was moved by Dr. J. W. Richards, and subsequently carried, that the reports be accepted.

The proposed amendments to the Constitution, as printed with the ballots of the annual meeting, were then adopted by resolution of the Society, as offered by Mr. Carl Hering.

AMENDMENTS TO CONSTITUTION.

ARTICLE IV to be amended as follows:

Section 2.—Words "annual meeting" to be stricken out, and "16th day of March" substituted.

Section 3.—Words "at an annual meeting" to be stricken out, and "by the 16th of March" substituted.

ARTICLE VI.

ELECTION OF OFFICERS.

1. The Secretary shall send to all members nominating blanks not later than the first of January, and nominations, not necessarily upon these forms, will be received by the Secretary not later than the first of February. He shall mail to every member before February 16th a printed list of all candidates thus nominated who have received more than 5 per cent. of the number of valid nominating ballots cast. The

voting need not be restricted to the names on this list. The Board of Directors may endorse those which it prefers, and if so, the published list shall state it. The voting shall be by secret letter ballot, the voter shall sign his name on an outside envelope, and the ballot shall be inclosed in an inner sealed and unmarked envelope. Ballots must reach the Secretary before the 16th day of March. The results of the election shall be announced at the annual meeting.

2. At the Directors' meeting to be held in February or March, the Board of Directors shall appoint three tellers who shall not be members of the Board of Directors, and three alternates. Should this Directors' meeting not be held, the President shall appoint these tellers, who shall be notified by the Secretary.

3. The tellers shall meet as soon after the 15th day of March as possible. The Secretary shall deliver to the tellers all ballots received by him, marking the outside envelopes received from members not entitled to vote. The tellers shall open only the envelopes not thus marked, and shall proceed in secret to count the votes received before the 16th day of March. All ballots and unopened envelopes shall be returned to the Secretary, who shall preserve them for one month. At the end of one month the Secretary shall return to the senders all rejected envelopes and shall open all unidentified envelopes. Cumulative votes shall count as one vote. The tellers shall prepare and sign a report of the results of the vote, which shall be sealed, and shall remain in the possession of the Chairman of the Committee, who shall hand this report to the presiding officer at the ensuing annual meeting. The presiding officer shall then cause this report to be read, and shall declare duly elected the eligible persons receiving the greatest number of votes for the respective offices.

ARTICLE VIII.

MEETINGS.

Section 1 to be changed to read:

1. The annual meeting shall be held during the last week of March or in April. Business affecting the organization of the Society shall be transacted only at the annual meetings. Proxy or mail votes shall be received.

PROCEEDINGS OF THE BOARD OF DIRECTORS

The only item of general interest to the Society passed upon by the Board during the period from September 16, 1904, to April 25, 1905, and not embodied in the Report of the Secretary as published herewith, is that the Faraday Society had discontinued its arrangement for publication with the *Electrochemist and Metallurgist,* and would in the future publish its Transactions quarterly. The exchange with our Society, however, has been continued.

The following papers were then read and discussed, as printed in full in the Transactions:

"Electrolytic Precipitation of Chromium," by H. R. Carveth.

"Electrolytic Precipitation of Silver," by R. C. Snowdon, read by Dr. Carveth.

"Some Results of Experiments with the Electrodeposition of Metals on Aluminum," by A. Lodyguine.

"Some Experiments with the Reduction of Titaniferous Ores into Steel and Titanate of Iron," by A. Lodyguine.

"The Specific Inductive Capacities of Certain Oleates," by Dr. L. Kahlenberg.

"The Rotating Diaphragm," by Dr. W. D. Bancroft, read by Dr. Carveth.

"The Heat of Solution of Aluminum Bromide in Ethyl Bromide," by Prof. H. E. Patten.

"On the Interdependence of Atomic Weights and Electrochemical Equivalents," by Prof. A. Reuterdahl.

"On the Utilization of Blast Furnace Gases in Connection with Electric Smelting," by A. J. Rossi.

"On the Reduction of Different Oxides of Lead by the Electric Current," by A. Lodyguine.

After adjournment for the day the members were received by President Eliot, and entertained for luncheon by Harvard University at Harvard Union.

President Eliot spoke of the great importance of a "borderland" science such as electrochemistry, in a brief but very pleasing address.

In the afternoon the Local Committee conducted an excursion to the New England Coke and Gas Company's plant at Everett, which was much enjoyed.

Session of April 27th.

The report of the tellers of election was read as follows:

Report of Tellers of Election.

For President—W. D. Bancroft, 130; Carl Hering, 66; E. G.

Acheson, 7; W. R. Whitney, 4; C. F. Burgess, 3; C. A. Doremus, 2, and L. Kahlenberg, 1.

For Vice-Presidents—E. F. Roeber, 157; Carl Hering, 88; L. Kahlenberg, 80; A. H. Cowles, 55; W. D. Weaver, 39; H. S. Carhart, 29; W. H. Walker, 21; F. A. J. FitzGerald, 20; A. E. Kennelly, 16; J. W. Richards, 16; F. J. Tone, 16; C. F. Chandler, 13; T. A. Edison, 9; C. P. Steinmetz, 10; D. H. Browne, 6; Henry Noel Potter, 6; C. E. Acker, 4; H. T. Barnes, 4; C. B. Dudley, 4; C. J. Reed, 4; E. G. Acheson, 3; W. J. Hammer, 3; C. A. Doremus, 3; W. D. Bancroft, 2; C. F. Burgess, 2; W. J. Hammer, 2; W. McA. Johnson, 2; C. O. Mailloux, 2; L. A. Parsons, 2; S. Reber, 2; A. J. Rossi, 2; P. G. Salom, 2; R. S. Hutton, 2; S. L. Bigelow, 1; E. Hart, 1; T. W. Richards, 1; E. R. Taylor, 1; H. Howard, 1; E. Weston, 1; W. R. Whitney, 1.

For Managers—C. A. Doremus, 127; C. P. Townsend, 94; W. R. Whitney, 79; W. McA. Johnson, 64; A. von Isakovics, 30; C. J. Reed, 23; A. H. Cowles, 18; H. M. Goodwin, 18; C. M. Hall, 17; W. E. Goldsborough, 15; F. J. Tone, 15; F. A. J. FitzGerald, 13; W. D. Bancroft, 12; F. M. Becket, 10; Henry Noel Potter, 10; N. S. Keith, 9; Carl Hambuechen, 8; E. A. Byrnes, 7; C. F. Mabery, 7; W. H. Wahl, 6; W. J. Hammer, 5; C. F. Burgess, 4; G. P. Scholl, 4; A. G. Betts, 3; D. H. Browne, 3; L. Kahlenberg, 3; J. W. Langley, 3; J. W. Richards, 3; J. W. Walker, 2; R. Fleming, 2; L. A. Parsons, 2; C. P. Steinmetz, 2; G. F. Brindley, 1; E. R. Taylor, 1; H. S. Carhart, 1; W. D. Weaver, 1; W. T. Taggart, 1.

For Secretary—S. S. Sadtler, 205; E. F. Roeber, 5; C. J. Reed, 1; blanks, 2.

For Treasurer—P. G. Salom, 207; blanks, 6.

President Carhart then declared the following officers elected for various terms:

For President—Dr. W. D. Bancroft, to serve for one year.

For Vice-Presidents—Dr. E. F. Roeber, Carl Hering and Dr. L. Kahlenberg, to serve two years.

For Managers—Dr. C. A. Doremus, C. P. Townsend and Dr. W. R. Whitney, to serve for three years.

For Treasurer—Pedro G. Salom, to serve for one year.

For Secretary—S. S. Sadtler, to serve for one year.

The following papers were then read, as printed in full in the Transactions:

"Electrostatic Method for Separating and Concentrating Ores," by Prof. Lucien Ira Blake, read by Mr. Locke.

"Colloids," by Dr. W. R. Whitney.

"An Electrolytic Switch," by W. S. Horry.

"The Production of Silicon in the Electric Furnace," by F. J. Tone.

"The Microstructure of Silicon and Silicon Alloys," by A. B. Albro.

"The Mercury Arc," by Dr. E. Weintraub.

"Electric Arcs," by Dr. W. R. Whitney.

"An Optical Method of Observing the Diffusion in an Electrolyte," by C. Hambuechen.

"Adherence of Nickel to Nickel," by R. C. Snowdon.

"A Low Voltage Standard Cell," by Prof. G. A. Hulett.

In the interval between the reading of the paper on "Silicon and Silicon Alloys," and that on the "Mercury Arc," a resolution of thanks was presented as follows:

Dr. J. W. Richards: In order to save a little time while Dr. Weintraub's apparatus is being put in place, I would like to transform the character of the proceedings to a vote of thanks to the Local Committee which has so splendidly done its work in the arrangement of this meeting; to the authorities of the Massachusetts Institute of Technology, to whom we are greatly indebted for the facilities which we have had; to the authorities of Harvard University, who have co-operated so willingly towards the success of our meeting; to the Everett Gas and Coke Company; to the General Electric Company, and to the Regents of Wellesley College for their kindness in showing their plants and many other interesting things to the Society and its guests.

Mr. Hering: I take pleasure in seconding that motion.

The President: I hope you have all heard the motion, gentlemen. It expresses the thanks of the Society for the labors of the committee and for the entertainment and hospitality of the Institute of Technology of Harvard University, and to the Regents of Wellesley College.

I am sure we must all heartily approve of this vote of thanks,

because we are greatly indebted to the persons and organizations mentioned in the resolution for the success and enjoyment of this meeting of the American Electrochemical Society. I will ask you, therefore, to approve of this resolution by the usual sign of Aye.

(An acclamation of "ayes" follows.)

President Carhart: I think the Society may congratulate itself upon the success of this Seventh General Meeting. The attendance, certainly both in quantity and in quality—especially in the latter—is very gratifying. A remark was made, I think, by some of the electrical journals at the time of the organization of this Society three years ago, when we were congratulated upon the quality of the papers presented at that first meeting, that it remained to be seen whether the Society would be able to keep up such a programme for successive meetings. Now I feel, personally, that the Society may certainly congratulate itself that the product, so to speak, has not been exhausted. It is not like a gas well or an oil well; it is not a pocket of papers on electrochemistry; but it seems to me the mills of the gods as represented by the electrochemists continue to grind, and I am sure the papers that have been presented at this meeting will compare very favorably in quality with those of any other meeting of the Society. I congratulate you, ladies and gentlemen, upon the success of this meeting from every point of view, and I now declare the Seventh General Meeting of the American Electrochemical Society adjourned.

After leaving the Lowell Building, the members of the Society and guests were entertained by the Local Committee for luncheon at the Technology Club.

The afternoon was spent in inspecting the Institute Buildings, particularly the Departments of Mining and Metallurgy, Electrochemical Engineering, and the new Research Laboratories.

RESOLUTION OF LADIES ATTENDING THE BOSTON MEETING.

The ladies attending the meeting of the American Electrochemical Society at Boston wish to place on record their appreciation

of the hospitalities extended to them and the courtesies shown by the Regents of Wellesley College, the authorities of the Massachusetts Institute of Technology and Harvard University, and most particularly by the resident Boston ladies, who contributed so unsparingly both time and effort in making our visit to Boston a memorable one.

MRS. J. W. RICHARDS,
MRS. E. R. TAYLOR,
Committee of the Visiting Ladies.

MEMBERS ELECTED NOVEMBER, 1904, TO MAY, 1905.

November 5, 1904.

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December 3, 1904.

I. Baum, Uniontown, Pa.; Dr. F. Winteler, Buffalo, N. Y.

January 7, 1905.

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February 4, 1905.

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March 4, 1905.

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April 1, 1905.

Daniel McMaster, Rumford Falls, Me.; Arthur D. Little, Boston, Mass.; Marten Hedlund, Hallstahammar, Sweden.

May 6, 1905.

W. H. Kimball, M.D., Portland, Me.; A. S. Ramage, Detroit, Mich.; J. M. Woodward, Washington, D. C.; C. A. Hansen, Madison, Wis.; Johns Woods Beckman, Tarentum, Pa.

OBITUARY SINCE APRIL, 1904.

E. K. Adams, elected April 3, 1902; died July 21, 1904.
J. W. Best, elected July 1, 1904; died August 20, 1904.
E. H. Mullin, elected April 3, 1902; died January 25, 1905.
C. M. Rosendale, elected April 2, 1903; died August 25, 1904.

Presidential address delivered at the Seventh General Meeting of the American Electrochemical Society, held at Boston, Mass., April 25, 1905, Vice-President Bancroft in the chair.

REVISIONS OF THE THEORY OF ELECTROLYSIS.

By Henry S. Carhart, LL.D.

No subject in the whole domain of theoretical electricity possesses more interest to the electrochemist than the theory of the decomposition of aqueous solutions of salts and acids through the agency of an electric current. For more than a hundred years scientific attention has been converged on it, for it has presented problems both of unusual interest and of unusual difficulty. Its development has not been one of uninterrupted progress, but rather one of leaps and bounds, alternating with seasons of suspended animation. Even with the noteworthy additions of the past twenty years, it cannot be said that all difficulties have yet been resolved. We are in little danger of so completely clearing up the entire field that nothing shall be left for posterity.

An historical review of this subject, biased it may be by perspective and distorted by the disproportionately large visual angle under which we view recent events, may yet give us more respect for the achievements of the past and less unreserved satisfaction with the advances of our own times.

The earliest record of observed electrolysis dates back of the invention of Volta's dry pile and "crown of cups." The decomposition of water by electrical means was described by van Troostwijk and Deimann in 1789. It was accomplished by sending a series of electric discharges through water in a narrow glass tube between gold wires whose ends were an inch and a half apart. The tube was placed vertically, and when the end of the upper wire became uncovered the spark caused the explosive reunion of the mixed gases. These experimenters concluded, contrary to the opinion of many of their scientific contemporaries, that both the hydrogen and the oxygen were obtained from the decomposition of water, and that water consisted of a union of these two gases only. They cited both the synthesis and the analysis taking place

in their experimental tube as proofs of their view. But the question as to the manner in which electricity acts to effect the decomposition remained unanswered. They did not obtain the two gases separately, but mixed in the glass tube. An enormous number of discharges were said to be necessary to produce an appreciable volume of mixed gases—14,600 for ⅓ cubic inch.

A little later Ritter found that 50 or 60 discharges from a Leyden jar through a solution of silver nitrate between silver wires gave a visible deposit of metallic silver on the negative electrode. By reversing the poles this deposit disappeared, and at the same time a new deposit formed on the other wire.

It is therefore obvious that the scientific world was prepared to accept electrolytic decomposition when Volta disclosed his invention of the dry pile and the voltaic battery, or "crown of cups." This disclosure was made in a letter to Sir Joseph Banks, president of the Royal Society of London, dated March 20, 1800. Before this letter was published in the Philosophical Transactions its contents had become known to London physicists, and Nicholson and Carlisle had decomposed water by means of Volta's pile. Carlisle made the acute observation that when a drop of water was placed on the upper plate of the pile to improve the contact between it and the wire of the external circuit, gas was given off; and Nicholson recognized the presence of hydrogen when the wire used was steel. These and similar facts induced them to send the electric current from a pile of 36 pairs through river water between brass wires in a glass tube half an inch in diameter. A fine stream of gas bubbles was at once given off from the negative electrode. One-fifteenth of a cubic inch was obtained in an hour and a half, and when this was mixed with an equal volume of air the mixture exploded on the approach of a lighted wax taper.

Although these observers expected the decomposition of water, they were not prepared for the astonishing fact that, while the hydrogen appeared at the exposed end of one of the wires, the oxygen appeared only at the end of the other, nearly two inches distant. This phenomenon was to its discoverers inexplicable. They made the very relevant and acute remark that this new phenomenon "appears to show perhaps a general law of the action of electricity in chemical processes." The explanation of this

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remarkable fact has ever since engaged the attention and best endeavors of science.

It is worthy of attention also that Nicholson and Carlisle observed that chemical action takes place in a voltaic cell when it functions as a source of current. In other words, they recognized that a voltaic cell is also an electrolytic cell. This is the first of many facts which tell against Volta's contact theory of the electromotive force of a voltaic cell. Volta himself asserted that the chemical actions going on in a voltaic cell have practically no essential significance.

In this same celebrated year of 1800 Cruikshank decomposed lead acetate between silver wires. A minute or two after connection was made, he observed lustrous metallic lead crystals on the negative electrode, while gas was released at the positive. Cruikshank called attention to the fact that only liquids containing oxygen conduct electricity, and he appears to have concluded that electricity seizes on the oxygen and transports it invisibly to the positive pole. Not so far removed from this conception is the present view that the oxygen conveys an electric charge rather than that the charge conveys the oxygen.

The separate appearance of the two products of decomposition at the electrodes was the most noteworthy and at the same time the most inexplicable fact of electrolysis to all the chemists and physicists of the day. An unknown correspondent in Nicholson's Journal expressed himself as follows: "I should like to inquire how it can happen in any system that the two components of water can be caused to appear at such a distance from each other. Does the hydrogen from the dissociated particles of water at the zinc side of the pile fly from it at the instant when the oxygen is liberated there? If that is so, why does not one see the gas bubbles on the way? Or does the oxygen migrate from the silver side to the zinc side? Or are there two streams at once?"

It should be remembered that Volta attached an extra zinc plate to the silver at the positive end and an extra silver plate to the zinc at the negative end, both in the case of his dry pile and crown of cups or voltaic battery. Hence in the early literature the zinc side means the positive and the silver the negative.

Sir Humphry Davy was early in the field of electric research,

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and at once distanced all his English confreres by the number and importance of his detail discoveries. In particular at the outset he obtained oxygen and hydrogen in different tubes separated in the circuit by the interposition of his own person as a conductor, and he proved conclusively that the two gases are evolved in the same relative proportion in which they exist as elements in water. But Sir Humphry Davy added little to the theory of electric action in electrolysis. Near the close of one of his papers published in December, 1800, he remarks:

"On these facts I shall not presume to speculate. . . . . Many new observations must be collected, probably before we shall be able to ascertain whether water is decomposed in galvanic processes. Supposing its decomposition, we must assume that at least one of its elements is capable of rapidly passing in an invisible form through metallic substances, or through water and many connected organic bodies; and such an assumption is incommensurable with all known facts. But a short period has elapsed since philosophers beheld with wonder, solid and fluid substances assuming new modes of existence in different gases. Do not the new phenomena of galvanism authorize us to hope that at no very distant time they will behold even those gases undergoing novel changes, and existing in new and now unknown forms?"

The diffuseness and lack of concreteness of ideas in those early days of the science before the time of Ohm's law are strikingly illustrated in the following extract from a syllabus of a course of lectures delivered by Davy in the theater of the Royal Institution in January, 1802:

"The agency of the galvanic influence which occasions chemical changes in water, and communicates shocks to the living body, is probably in some measure distinct from that agency which produces sparks, and the combustion of bodies. The one appears, all other circumstances being similar, to have little relation to surface in compound circles; but to be great in some unknown proportion as the series are numerous. The intensity of the other seems to be as much connected with the extension of the surface of the series, as with their number." Davy was not at that time able to distinguish between electromotive force or electric pressure and strength of current.

The long contest waged between the supporters of the contact theory of electric action in a voltaic couple and the chemical theory is briefly alluded to in this same syllabus without any clear intimation of the position taken by Sir Humphry himself:

"M. Volta has supposed that an electrical current is always produced by the mere contact of certain different conductors of electricity. But many of the British philosophers have denied this position; accounting for galvanism from the destruction of the equilibrium of electricity in galvanic circles, in consequence of the chemical agencies of the different bodies composing them."

On November 20, 1806, Davy read before the Royal Society a Bakerian lecture on "Some Chemical Agencies of Electricity." In this lecture he takes a decided position against the chemical theory of electrical excitation held by many British philosophers. He says: "The general ideas advanced in the preceding pages are evidently directly in contradiction to the opinion advanced by Fabroni, and which, in the early stages of investigation, appeared extremely probable, namely, that chemical changes are the *primary* causes of the phenomena of galvanism."

"Before the experiments of M. Volta on the electricity excited by the mere contact of metals were published, I had to a certain extent adopted this opinion; but the new facts immediately proved that another power must necessarily be concerned."

In this same lecture we find suggestions by this distinguished philosopher harmonizing with the celebrated theory of Grotthus; but no credit is due to Davy for these suggestions, because Grotthus published his theory in the year 1805 in Rome, under the title: "Memoire sur la decomposition de l'eau et des corps, qu'elle tient en dissolution, a l'aide de l'électricité galvanique." A second edition followed the next year, and the memoire was also published in the Annales de Chimie in 1806. Sir Humphry says:

"It is very natural to suppose that the repellent and attractive energies are communicated from one *particle to another particle* of the same kind, so as to establish a conducting chain in the fluid; and that this is really the case seems to be shown by many facts. . . .

"In the case of the separation of the constituents of water, and of solutions of neutral salts forming the whole of the chain, there

may possibly be a succession of decompositions and recompositions throughout the fluid."

Ostwald says (Elektrochemie, p. 307) that the different theories proposed to explain the separate evolution of the products of electrical decomposition vied with one another in improbability; and no one of them was free from the most serious objections. When at length one view met with general acceptance, it was not so much because of its unconditional excellence as because it was at least relatively the best of all.

Hear the account of Grotthus himself relating to the origin of his theory. He says: "Volta's pile, which made the genius of its inventor immortal, is an electrical magnet, of which each element (that is, each pair of plates) has both a positive and a negative pole. The consideration of this polarity has suggested to me the idea that a similar polarity might form between the molecules of water, when it is acted on by this same electrical agent; and I must confess that this was for me a gleam of light."

Freiherr von Grotthus was a most interesting character. At the age of a year and a half the death of his father left him to the care of his mother, and he lived with her on her landed estate in Lithuania, near the borders of the Baltic province of Kurland, till his seventeenth year. The taste for science developed in him at an early age, but it was stifled in the most brutal and unsympathetic manner by his teacher, who had neither the taste nor the intelligence for the studies to which the genius of Grotthus inclined. In the year 1803, at the age of eighteen, he went to Leipzig to study, and after six months there he betook himself to Paris, where he listened to the lectures of the most distinguished philosophers of the time. The threatened war between France and Russia compelled him to leave Paris, and he hastened to Naples, where he remained till the end of the year 1805. Through his fortunate acquaintance there with a distinguished English physician named Thomson, who was the owner of a small galvanic apparatus, our young natural philosopher was enabled to repeat the experiments of Professor Pacchiani, which were then exciting much attention. The result was his theory of electrolysis, first published in 1805, when its author was not more than twenty years of age—a theory which held sway for nearly three-quarters of a century, and which has forever linked his name with the history of electrochemistry.

Under more favorable conditions of birth, education and surroundings, Grotthus might have become one of the most distinguished investigators of his time. But in the autumn of 1807 he felt compelled to return to his ancestral estate, and to busy himself with the duties of manager. Here in the country, in a remote angle of Lithuania, for the most part without literary associates, and lacking often the most essential means of research, he wrung from Nature some of her well-concealed secrets, and wrote nearly all his contributions to science.

For years he suffered unspeakably from an incurable organic malady. The trouble increased from day to day, and finally reached such an acute stage that he was brought to the rash decision to sever voluntarily the thread of life. He died in 1822 at the age of thirty-seven.

The Grotthus theory of the mechanism of electrolysis does not respond, as we now know, to the facts of later discovery. But since for the first time it made comprehensible the physical possibility of the phenomena of electrolytic decomposition, it has enduring value.

Grotthus conceived that a species of polarization is set up in the water by electrical agency, so that the positively charged elements are turned toward the negative electrode, and the negatively charged ones in the other direction. Also, that at the moment of separation of the oxygen and hydrogen from each other, a division of their natural charge of electricity takes place in some way not explained. Attractions and repulsions follow; also the continuous movement of two streams of charged particles in opposite directions, through the process of molecular interchanges, or the exchange of partners whose conjugal bond is chemical affinity. Grotthus does not appear to have got the conception that a current in an electrolyte is the convection of positive and negative charges in opposite directions, but his theory was directed toward the explanation of the most obvious and novel fact that the products of the decomposition appear at widely distant points. He distinctly remarks that the process, as he conceives it, involves decomposition at the electrodes only, where the current passes between the electrode and the electrolyte. He says: "I conclude, therefore, that if it were possible to produce in water a current of galvanic electricity, so that it should describe in it a

complete circuit, all the molecules of the liquid, which are in this circuit, would at the same instant be decomposed and again reformed; whence it follows that this water, although it underlies the action of galvanism, would still always remain water."

Grotthus had no consistent idea of the relation between the charges carried by the components of a molecule and the passage of a current. The current appeared to him only to align the molecular components, and the resulting molecular cleavages and re-formations were due to the attraction and repulsion between the electric charges, or their polarity. His conception was crude and imperfect compared with the corresponding concepts of the present time. But it showed at least that the phenomena of electrolysis takes place by a conceivable process. If it did not satisfy all intellectual demands, it quieted clamor and bridged the gulf between the known and the inexplicable. It was indeed a gleam of light that has never been effaced; and we owe an everlasting debt of gratitude to the farmer philosopher of Lithuania.

Grotthus gave a vivid picture of the chief phenomenon of electrolysis, the appearance of the separated constituents at the electrodes only. The knowledge of his time scarcely reached beyond this one fact. It was not long, however, before new observations were made, which could with difficulty be fitted into his picture.

The essential fact which the theory of Grotthus was incompetent to answer satisfactorily was that the smallest electromotive force may produce a current through an electrolyte, and the strength of this current follows Ohm's law.

Grotthus assumes that the application of an electromotive force to the electrodes gives rise to a polarized condition of the molecules, and that at the instant of the separation of the hydrogen and oxygen, for example, a separation of their natural charge of electricity takes place, either through contact or friction; so that one part becomes electropositive and the other electronegative. This perhaps means that the normal condition of an electrolyte is one of equilibrium with rigidly combined molecules. Grotthus did not appear to conceive of the cleavage of a polarized molecule until current passed.

From the time of Grotthus there was a long pause of fifty years

in the theory of electrolysis, for no important step was taken until Clausius in 1857 published his profound modification of the Grotthus theory. Clausius' study of the kinetic theory of heat prepared him to apply similar principles to the interpretation of electrolytic phenomena. He leaves no doubt about his meaning; his conceptions are always clear and clearly expressed. I will let him speak for himself.*

"Let there be a liquid, consisting wholly or in part of electrolytic molecules; and let it be assumed that these molecules are arranged in the natural condition of the liquid in any definite manner in which they persist, so long as no foreign force acts on them, while the individual molecules oscillate perhaps about their positions of equilibrium, but are unable to get quite away from them. Further, let an attraction be assumed between two part-molecules, as there must be in every possible arrangement, and let two part-molecules be bound together into a whole molecule and, therefore, very near together; then the attraction binding them together is greater than the attraction between the positive part-molecule of one complete molecule and the negative of another. If now an electric force acts within this mass, and seeks to urge the positively electrified part-molecules in one direction and the negatively electrified ones in the other, then the question arises what influence this electric force must exert on the behavior of the molecules."

"Inasmuch as the molecules are assumed to be capable of rotation, the first effect would plainly be to turn all of them in the same manner, so that the two oppositely electrified portions of each complete molecule would be turned in the direction in which they are urged by the acting force. Further, the force would seek to separate the part-molecules, united in a whole or complete one, and to move them in opposite directions; and if this motion ensues, then the positive part-molecule of one whole one would meet the negative of the following and would combine with it. But now, in order that the once united part-molecules may be separated, the attraction which they exercise on each other must be overcome. Therefore a force of definite strength is necessary, and one is thus led to the conclusion that, so long as the force acting on the conductor does not have this strength, no

* Annal d. Physik, Vol. 101, 1857.

decomposition whatever can take place; and that, on the contrary, if the force is increased to the requisite strength, very many molecules must be decomposed at the same time, since they are all under the influence of the same force, and have precisely the same relation to one another."

"With respect to the electric current, the conclusion can be expressed as follows, if it is assumed that the conductor conducts only through electrolysis. So long as the force acting on the conductor is below a certain limit, it will produce no current whatever; but if it has reached this limit, then suddenly a very strong current will flow. But this conclusion is flatly contradicted by experience. Even the smallest force causes a current, conducted by alternate decompositions and reunions, and the intensity of this current increases in accordance with Ohm's law in proportion to the electromotive force."

"It follows from these considerations that the above supposition, to the effect that the part-molecules of an electrolyte are bound together in the fixed relation of whole molecules, and that these have a definite and regular arrangement, must be untrue."

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"I believe therefore that the following hypothesis, by which this contradiction is removed, and which, as it seems to me, is in harmony with other known facts, deserves some consideration:

"In my treatise 'On the Mode of Motion, which we call Heat,' I have expressed the view that in liquids the molecules have no definite positions of equilibrium, about which they only oscillate, but that their motions are so lively that they thereby constantly come into entirely changed and new relations to one another, and move among one another in an irregular way."

"Let us now imagine in an electrolytic liquid a single part-molecule present, for example, an electro-positive one, the electrical condition of which we shall assume is exactly the same as at the moment when it was separated from a complete molecule. I believe now that while this part-molecule moves about among the whole molecules, under the many relations which it can assume, sometime those will occur in which it will attract the negative part-molecule of an undissociated molecule with greater force than that with which the two parts belonging to an undissociated molecule, whose relation to each other is not entirely

unchangeable, attract each other at this same instant. As soon as this condition occurs it will join itself to this negative part-molecule, and the positive part-molecule formerly bound to the same thereby becomes free. This one now in turn moves about free, and after a time decomposes another whole molecule in the same manner, and so on. All these movements and decompositions occur in the same irregular manner as the heat motions by which they are set going."

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"When now in a liquid, whose molecules already find themselves in such motion that they exchange their part-molecules in an irregular way, an electric force acts, which tries to drive all the positive part-molecules in one direction and the negative ones in the opposite, then it is easy to understand what differences in the mode of the molecular movements must ensue."

"A free part-molecule will then no longer follow the irregularly changing directions, which it is forced to pursue by the heat motions, but it will change the direction of its motion to correspond with the acting force; so that, although the motions of the positive part-molecules are very irregular, still a certain direction will prevail among them; and likewise the negative part-molecules will move under compulsion in the opposite direction."

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"If one considers within a liquid on which an electric force acts a small surface at right angles to the direction of the force, then through this area more positive part-molecules pass in unit time in the positive direction than in the negative, and more negative part-molecules in the negative than in the positive direction; . . . . so that a certain excess number of positive part-molecules go in the positive direction and a certain excess number of negative part-molecules in the negative direction through the small area. The magnitude of these two numbers does not need to be the same, since it depends also, outside of the force urging them, which is the same for both, on the degree of their mobility, and this may for many reasons be different for different part-molecules."

"These opposite movements of the two kinds of part-molecules compose the voltaic current within a liquid."

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"By this conception of the state of liquids the difficulty mentioned above vanishes. It is readily seen that the influence which the electric force exerts on the irregular molecular decompositions and motions already existing does not begin when the force has reached a certain value, but that even the smallest force must act on them, and that the amount of this action must increase with the magnitude of the force. The entire process then agrees well with Ohm's law."

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"If we compare the older Grotthus theory with the one here developed, the difference lies chiefly in this: in the former it was assumed that the motion is first brought about by the electric force, and takes place in two definite directions only, while the decompositions go on regularly from molecule to molecule; but in the latter the motions already present are only modified, not to the extent of making them entirely regular, but only so that among the great multitude of motions those in the two definite directions prevail."

These ideas of Clausius are so fundamental in the modern theory of electrolysis that I have thought it best to translate them freely, rather than to paraphrase them. Clausius belongs to our own day. The gray hair and benign expression of this beautiful old man made a lasting impression on me as I saw him at the International Electrical Congress in Paris in 1881.

Grotthus conceived of the motion of the part-molecules as taking place under electric force only by the progressive exchange of partners in a polarized chain of molecules. Clausius rejected the fixed equilibrium in the normal condition of an electrolyte, and assumed some free part-molecules or, as Faraday named them, ions; and the dissociation imagined by Clausius may be described as temporary, or a continuous exchange of partners in chemical association. Williamson as early as 1851 declared "that in an aggregate of the molecules of every compound a constant interchange between the elements contained in them is taking place." This view Clausius rejected. The assumption that only a few of the molecules in a solution are dissociated into ions appeared to him to satisfy the facts of electrolysis.

The first attempt to answer the question as to the manner in which the facts of electrical conductivity are reconciled with those

of general chemistry was contained in the theory of Grotthus; the second attempt was made by Clausius in 1857; and thirty years later a further answer was made in the work of Arrhenius.

Another question relates to the intimate relation between the passage of electricity through an electrolyte and the simultaneous motion of the ions, the ponderable attendant of the electrical transfer. The law of Faraday paved the way for an answer to this question; the reply of the present is largely the work of Hittorf and of Kohlrausch.

The simplest statement of Faraday's discovery in electrolysis is that the passage of a fixed quantity of electricity is always associated with the transfer of a gramme equivalent of the ion. The passage through an electrolyte of 96,550 coulombs of electricity always releases or deposits a gramme equivalent of an ion, that is, a gramme molecule of an ion whose valence is one, or half a gramm molecule of an ion whose valence is two. This law demonstrates that there is a fixed minimum, called by Helmholtz *the atomic charge,* conveyed by univalent ions, others conveying only integral multiples of this charge.

The researches of Hittorf on the migration of ions demonstrated that the observed change in concentration at the electrodes during electrolysis makes it necessary to assign to the positive and negative ions different velocities. Hittorf's work, though of fundamental importance, commanded but little attention at the time of its publication; in fact it was opposed by the leaders of physical science and was not accepted till thirty years later.

Let me now recount several steps in the revision of electrolytic theory:

Grotthus supposed "that at the moment of the segregated appearance of the hydrogen and oxygen there takes place a division of their natural electricity, either by their contact or by mutual friction, so that the former assumes the positive, the latter the negative condition," and that the links of his chain exchanged partners in such a way as to leave only the end links free.

Clausius assumed "that the ions are not permanently united with each other; that part of them exist in the liquid in an uncombined state, wandering about seeking partners." The electric force imposes on all free ions a uniform drift. To Clausius,

therefore, should be assigned the introduction of the theory of dissociation to explain electrolysis. But the dissociation of Clausius was only slight and was conceived to be the accompaniment of a shifting and unstable equilibrium.

Scientific judgment respecting the assumption of Clausius remained in abeyance for thirty years, when Arrhenius published his celebrated memoir on "The Dissociation of Substances Dissolved in Water." An intermediate step, not originally devoted to the theory of dissociation was Van't Hoff's paper on "The Rôle of Osmotic Pressure in the Analogy between Solutions and Gases." The significant feature of this paper is the generalization of Avogadro's law to the effect that—

"The pressure which a gas exerts at a given temperature, if a definite number of molecules is contained in a definite volume, is equal to the osmotic pressure which is produced by *most substances* under the same conditions, if they are dissolved in any given liquid."

The major part of Van't Hoff's paper deals with non-electrolytes or organic compounds, such as a solution of sugar, which show little or no deviation from Avogadro's law as applied to osmotic pressure. When he alludes to those substances which exhibit abnormally large osmotic pressure, he acknowledges his indebtedness to the personal suggestion of Arrhenius to the effect that the solutions obeying the law of Avogadro are non-conductors of electricity, a fact indicating that they are not broken down into ions, while solutions which give higher values of the osmotic pressure than accord with the laws of gases are all electrolytes. But if these suffer partial dissociation in solution, then the number of particles is increased, each ion contributing to the pressure as much as a complete molecule. The excessive osmotic pressure is thus accounted for.

Arrhenius divided the molecules in a conducting solution into active and inactive portions; the former are those whose ions are independent of one another in their movements; the latter are the remaining molecules whose ions are firmly bound to each other, and the ration between the two he called "the activity coefficient."

The significant conclusions of Arrhenius are:

1. "That Van't Hoff's law holds not only for *most,* but for *all*

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substances, even for those which have hitherto been regarded as exceptions (electrolytes in aqueous solution)."

2. "That every electrolyte (in aqueous solution) consists partly of active (in electrical and chemical relation) and partly of inactive molecules, the latter passing into active molecules on increasing the dilution, so that in infinitely dilute solutions only active molecules exist."

The ratio of the active to the inactive molecules, or the activity coefficient, is intimately connected with the electrical conductivity of solutions. Molecules dissociated into ions are alone capable of conducting or conveying electricity through a solution. The inactive molecules are at best only inert and take no part in the electrical transport. The activity coefficient increases with the dilution; that is, the molecular conductivity, which expresses essentially the conductance of a given number of molecules in solution, is greatest when the dilution is such that all molecules of the solute are dissociated. This is the essential significance of the researches on electrolytic conductivity, so far as they bear on the theory of electrolysis.

The transition from the incidental and almost infinitesimal dissociation assumed by Clausius to the ideal infinite dilution and complete dissociation taught by the "Leipzig School" marks the essential revision of the theory of electrolysis made in recent years.

The theory of ionization has now passed beyond the bounds of electrolytic solutions. As Van't Hoff imported the gas law into solutions to explain osmotic pressure, so others, like J. J. Thomson, have seized on electric convection by ions to explain electrical discharges through gases. It is now conceded that the only tenable explanation of electric currents through gases is that of convection by ions. The ionization of gases is brought about by ultra violet light, by Roentgen rays, and by the radiations from radio-active substances. The electric charge conveyed by ions in gases appears to be identical with the charge conveyed by ions in an electrolyte in aqueous solution, but the masses conveying negative charges are only about the one-thousandth part of the hydrogen ion.

The passage of electricity through a gas, as well as through an electrolyte, is accompanied by chemical changes; and chemical

decomposition, says J. J. Thomson, is not to be considered an accidental attendant on the electrical discharge, but an essential feature without which it could not occur.

In reviewing the changes that have occurred in the theory of electrolysis I would not be understood to imply that we now have the ultimate truth. Many cogent objections have been urged against the theory of dissociation in its present form. Theories should be regarded as helps or scaffolds only; they are necessary for the construction of the edifice of truth, and they finally disappear like the staging. We should use them as temporary expedients, not retaining them till the whole edifice is completed, but only until a grand arch is finished, some minaret or tower emerges against a clear sky, or light streams through some noble window.

The physicist or chemist, who is more intent to ascertain the truth than to preserve consistency, holds to a theory no longer than he finds it able to furnish support. Faraday, the prince of research, said that experimental work is a great disturber of preconceived theories.

Just now the dissociation theory is in a state of siege, with many valiant defenders. The objection is urged that there are many cases of electrolytes in solution in which the osmotic pressure does not exceed that required by the gas law. Hence there can be no dissociation. Also that the simplest cases of electrolysis are those of a molten salt, such as silver electrodes in molten silver chloride. In these cases there is no complication with a solvent and no dissociation by solution. In what way, then, is that migratory freedom of the electrically charged part-molecules, which is assumed in the theory of dissociation, secured in a molten salt? Dr. Kahlenberg has shown that "a normal solution of trichloracetic acid in allyl mustard oil is a poorer conductor of electricity than the purest water which Kohlrausch ever prepared in contact with air, and yet this solution attacks dry magnesium rapidly, and decomposes dry carbonates of sodium and potassium." But chemical reactions are assumed to depend on dissociation into ions, as does electrical conductivity.

This much is generally accepted: "The ions must be free to move; but this migratory freedom may be secured either by ionic interchanges between the molecules, as Clausius imagined, or by

a prolonged separation in accordance with the dissociation hypothesis of Arrhenius and Planck. The essential point in the general ionic theory is the migratory freedom."

The solution of obscure problems like those of electrolysis, in which even the chief agent itself is an elusive enigma, is necessarily one of prolonged effort, with many a flamboyant processional and the not infrequent refrain of the later recessional. But there is no occasion for discouragement, for we are destined to struggle forever with the unsolved problems of the here and the hereafter.

It is often darkest just before the dawn. Sometimes, too, we emerge into the light with a suddenness that blinds before the eye adjusts itself to the new illumination. One dreary day in April I took the train in Switzerland over the St. Gotthard route. We entered the north end of the tunnel at Goeschenen with a clouded sky and snowflakes swirling through the air. Ten minutes passed in the darkness a thousand feet beneath the village of Andermatt—fifteen, seventeen, and then the train ran out on the Italian side of the great divide at Airola into a burst of sunshine and clear sky and white-capped Alpine peaks and tempered winds and the pale green of olive groves. So sudden was the transformation that an involuntary exclamation of surprise and delight ran through the train. The experiences of the last twenty years warn us that we must be prepared for similar surprises in the illumination that physical science is shedding on the world of nature. We need not prophesy; we need only work and wait.

A paper read at the Seventh General Meeting of the American Electrochemical Society, held at Boston, Mass., April 25, 1905. President Carhart in the chair.

REVERSIBLE AND IRREVERSIBLE ELECTROLYTIC POLARIZATION.

W. S. Franklin and L. A. Freudenberger.

The various quantitative ideas which are employed in the discussion of physical phenomena from the point of view of thermodynamics, such as pressure, volume,[1] temperature and entropy, apply primarily to states of thermal equilibrium, but these quantitative ideas may be generalized so as to be strictly applicable to what are called permanently varying states.[2]

In the application of the principles of thermodynamics to actual phenomena, to things which really take place, it is essential either (a) that the processes involved approach complete reversibility as they take place more and more slowly (in which case the inferences drawn from a thermodynamic discussion apply to the continuous series of states of equilibrium which make up the reversible processes), or (b) that the processes involved approach more and more nearly to what may be called *steady sweeps*[3] as the actual physical conditions approach more and more nearly to the ideal conditions which are assumed to exist as a basis for the application of the ideas of thermodynamics.

The method used by Duhem for treating phenomena associated with what he calls false equilibria,[4] does not satisfy either of the above conditions. It seems probable, however, that what Duhem calls a state of false equilibrium (*e. g.,* free oxygen and hydrogen standing together in a vessel at ordinary room temperature) is

[1] The volume of a turbulent region is a measurable property of the quiescent envelope. That is to say, the measurement of the dimensions of a turbulent region can be carried out only in a quiescent bounding region. This bounding region may, indeed, be temporarily projected through the turbulent region in the form of carefully protected measuring standards, as exemplified in base line measurements, but the limits of the measured dimensions must always lie in a quiescent bounding region which is not devised for the immediate purpose of measurement, but whose independent and more or less permanent existence gives occasion for the measurement and value to the result.

[2] See Science N. S., Vol. XVIII, p. 656, November, 1903.

[3] See Science loc. cit., p. 648.

[4] Traité Elementaire de Mechanique Chimique, Vol. I, p. 201-295, Paris, 1897.

a case of an excessively slow and steady sweeping process which cannot be distinguished by careful observation from an unvarying state.

In a study of the phenomena of electrolysis a thing of first importance is to determine within the limits of experimental precision whether the process approaches complete reversibility as it is made to take place more and more slowly. The great difficulty encountered here, aside from the difficulty of approaching a limit by experimentation, is that subsidiary actions take place during electrolysis (diffusion, local action, etc.). The ordinary point of view is to consider that these subsidiary actions may be legitimately treated as actions which are independent of the main phenomenon of the deposition and discharge of the ions on the electrodes by the current, so that the effects of these subsidiary actions may be determined and separated from the effects of the ideally simple process of electrolysis,[5] but everyone who has worked at the determination of critical voltages, for example, knows how difficult it is to separate the aggregate of effects in electrolysis into those parts which may be ascribed to independent subsidiary actions, and those parts which may be ascribed to an ideally simple electrolytic process. It may be asked what is meant by an ideally simple elecrtolytic process and by ideally independent subsidiary actions. Indeed, such expressions may be strongly objected to, but it is greatly helpful, nevertheless, to give more or less concrete form to the hypotheses which serve to guide the choice of experimental conditions, with a view of separating observed effects into parts which correspond more or less definitely to certain aspects of the conditions under which the effects are obtained.

When electrolysis takes place rapidly one would naturally suppose it to be reversible. The investigation of this irreversible aspect of rapid electrolysis is the object of the experimental part of this paper.

[5] A similar case arises in the thermodynamic treatment of thermo-electric phenomena. The conduction of heat from hot to cold junctions always takes place alongside of the thermo-electric phenomena, and the application of thermodynamics to the thermo-electrc phenomena is based upon the idea that the thermo-electric phenomena are independent of the phenomena of heat conduction, that is to say, on the idea that the electrical aspects of the whole aggregate of phenomena may be changed at will without altering the accompanying phenomena of heat conduction and that the conditions which determine the magnitude of heat conduction may be changed at will without altering the accompanying electrical phenomena, an idea which is justified by such meagre experimentation as has been made hitherto to determine the question.

The attempts which have been made to determine critical voltages of decomposition of various electrolytes[6] have been essentially attempts to determine the reversibility of electrolysis when the current is made very small, but the experimental difficulties which have been encountered in this work have been very great, and the existence of critical voltages is still considered questionable by many.[7]

This question of the reversibility of slow electrolysis may, perhaps, be attacked most satisfactorily by choosing a form of electrolytic cell in which the driving electromotive force must approach zero as the current approaches zero if the action is reversible. This aspect of the problem has been dealt with by Mr. Barry MacNutt.[8] The experimental work in this case is also greatly complicated by subsidiary actions, such as changes of concentration of the electrolyte and changes in the character of the surface layers of the electrodes, and the result of Mr. MacNutt's work can only be said not to indicate that the voltage is other than zero when the current is vanishingly small.

Caspari[9] has studied the cathode polarization in the electrolysis of sulphuric acid when the current is barely large enough to produce visible generation of hydrogen. Caspari's results seem to show that cathodes of the different metals show characteristic excess-voltages (Uberspannungen), that is, voltages in excess of the value corresponding to the reversible liberation of hydrogen. This excess-voltage or over-voltage is nearly zero on spongy platinum and about three-quarters of a volt on zinc and on pure mercury.

Professor Ostwald and Dr. Bredig have suggested explanations[10] of Caspari's results. Professor Ostwald's explanation is that the first appearance of hydrogen in the form of excessively minute bubbles depends upon a high degree of supersaturation of dissolved hydrogen in the electrolyte near the cathode, and Dr. Bredig's explanation is that the electrolysis builds up from the hydrogen and the electrode metal, or from the hydrogen and the electrolyte, compounds which possess a great deal of free

[6] Helmholtz, Wied. Ann., *34*, p. 735 (1888). Le Blanc, Zeit. f. Phys. Chem., *8*, p. 299 (1891), and *12*, p. 333 (1893). Neumann, Zeit. f. Phys. Chem., *14*, p. 193 (1894). Nernst. Ber. d.d. Phys. Ges., *30*, p. 1553 (1897).

[7] A. Göckel, Zeit. f. Phys. Chem., *32*, p. 607 1900).

[8] Phys. Rev., *8*, p. 237 (1899).

[9] W. A. Caspari, Zeit. f. Phys. Chem., *30*, p. 89 (1899).

[10] Zeit. f. Electrochemie, *6*, p. 39-41 (1899).

energy (Helmholtz's *freie Energie*). In both cases the immediate results of the electrolysis would be such that the work done could be regained if it were not that the state of supersaturation in the one case is unstable and quickly collapses, and that the assumed free-energy compounds in the other case are unstable and immediately break down. That is to say, the electrolytic action, with the immediately accompanying actions at the electrodes, may be reversible, and only those independent actions which are really subsequent to the deposition irreversible. The method employed by the authors in the experimental part of this paper is capable of determining this question as to whether Caspari's overvoltages are due to irreversible processes associated with the fundamental electrolytic process or due to fundamentally reversible processes, as suggested by Professor Ostwald and by Dr. Bredig, provided, of course, that a finite time elapses between the building up of the unstable states by reversible electrolytic action and the irreversible collapse of these states independently of electrolytic action. Experiments touching this point are now under way.

A problem analogous to this of the reversible deposition of the ions in electrolysis is the question of the reversibility of the process of crystallization when it takes place slowly. Indeed, this process is always assumed to be reversible in the thermodynamic treatment of the separation of substances into distinct phases, but we know that in the rapid disolution of a crystal the crystal passes through a series of forms very different from the forms through which it passes during its growth. No direct experimental evidence has ever been brought to bear upon the question of the reversibility of slow growth and slow dissolution of crystals. It may be that the consistency of the results of thermodynamic theory, based upon the assumed reversibility of such processes as slow crystallization and slow electrolysis, is a sufficient indication as to the facts, but it seems desirable to approach the subject by direct experimentation, even though complete reversibility can never be experimentally demonstrated. One of the authors of this paper carried out some experiments on the reversibility of crystallization in 1893, but without definite results.

"The work spent in forcing a current through an electrolytic cell consists mainly of three parts:

"*(a)* The work which appears as heat throughout the electrolyte. The rate at which work is so spent—that is, the rate of generation of heat throughout the electrolyte, is accurately proportional to the square of the current.

"*(b)* The work which appears as heat at the electrodes on account of the irreversible processes, or sweeping processes, which take place as the ions are deposited. The rate at which work so expended is a function of the current, and it may be represented by φ (i).

"*(c)* The chemical decomposition of the electrolyte by the current requires work, and the reaction of the liberated ions upon the solvent or upon the electrodes is often a source of energy. The net rate of expenditure of energy in these ways is proportional to the current—it may be either positive or negative. Work gained or spent in an electrolytic cell on account of thermo-electromotive forces or on account of electromotive forces at places where the electrolyte changes in concentration or in composition may be included in this item (c).

"Let a current i be forced through an electrolytic cell by an electromotive force E. The rate at which work is done upon the cell is Ei. The rate at which energy appears as heat throughout the electrolyte is Ri_2. The rate at which energy appears as heat at the electrodes is φ *(i)*, and the rate at which work is spent in producing the chemical action is ei. We have, therefore:

$$Ei = Ri^2 + \varphi\, 2(i) + ei \qquad (1)$$

$$\text{or } E = Ri + f(i) + e \qquad (2)$$

in which R is the resistance of the electrolyte, e is the proportionality constant mentioned in item *(c)* above, and f *(i)* is written for φ (i)/i. The second equation shows that the electromotive force E which acts upon an electrolytic cell may be resolved into three parts, namely Ri, $f(i)$ and e." [11]

The polarization of an electrolytic cell may be defined as the back electromotive force of the cell aside from that part, Ri, which is due to the resistance of the electrolyte. That is, according to equation 2, the polarization may be defined as $-[f(i) + e]$, and it is equal and opposite to $(E - Ri)$, where E is the total electromotive force applied to the cell.

[11] Taken from Nichols and Franklin's *Elements of Physics*, Vol. II, p. 74, first edition, The Macmillan Co., New York, 1896.

That part of the polarization, or back electromotive force, of an electrolytic cell which persists when the current is reversed contributes to the recovery of the energy previously expended in the cell. This part of the polarization may therefore be called the reversible polarization of the cell. In general, the reversible polarization of an electrolytic cell may be defined as that part of the polarization which is not a function of the current. It must be remembered, however, that the value of the reversible polarization varies with concentration changes of the electrolyte, with changes in the character of the surface layers of the electrodes, and with temperature changes, due to a continued flow of current. These things are not, however, functions of the current, but they are functions of the time integral of the current, or the electric charge which has passed through the cell, and the portion of the reversible polarization which depends on these things does not change with quick changes of the current.

That part of the polarization of an electrolytic cell which does not persist when the current is quickly reversed, does not, of course, contribute to the recovery of the energy previously expended in the cell. This part of the polarization always, in fact, opposes the current and causes the dissipation of energy, and it may therefore be called the irreversible polarization of the cell. In general, the irreversible polarization of an electrolytic cell may be defined as that part of the polarization which is a function of the current.

It is by no means definitely known that there is irreversible polarization of an electrolytic cell. Caspari's results do not prove the existence of irreversible cathode polarization in the slow deposition of hydrogen ions, inasmuch as Caspari's results may be explained on the basis of reversible electrolytic actions. As to the existence of irreversible polarization when the electrolysis is rapid (current finite), it seems *a priori* probable that it does exist because every natural phenomenon which takes place at a finite rate is thermodynamically irreversible. The object of the experimental part of this paper is to determine whether irreversible polarization does exist in rapid electrolysis and to determine its value.

It may be of interest to point out some mechanical analogies illustrative of reversible and irreversible polarization.

Any reversible force which opposes a change in the state of a system is either a constant (independent of both velocity and configuration), or a function of the configuration of the system. Thus the force of gravity, which will give back all the work spent in overcoming it, is constant; the elastic reaction of a spring, which will give back all the work spent in overcoming it, is a function of the configuration of the spring. In so far as energy is dissipated in the distortion and release of a spring, forces are involved which are not functions of the configuration of the spring, forces which, for example, may be due to the viscosity of the metal, and which are therefore functions of the velocity of change of the system.

Any force which is a function of the velocity of change of a system depends upon actions which are thermodynamically irreversible. Thus the force of friction which opposes the sliding of one body over another is a function of the velocity. The force with which water opposes the motion of a boat is a function of the velocity.

The most familiar example of irreversible action in an electric circuit is the generation of heat in accordance with Joule's law, in which case the opposing electromotive force, Ri, is a linear function of the current.

In electromagnetic theory electric charge q (time integral of electric current) is a generalized co-ordinate which enters into the specification of the configuration of a system, and reversible electromotive forces may be functions of the electric charge which has passed through an electric circuit. The simplest example is the electromotive reaction of a charged condenser. Electric current, on the other hand, is a generalized velocity, and reversible electromotive forces cannot be functions of current.

The experimental part of this paper deals with that part of the electromotive force which opposes the flow of current through an electrolytic cell, which is a function of the current, not counting, of course, the well-known part Ri. This part is represented by $f(i)$ in equation 2, and we have called it the irreversible polarization of the cell.

It would, of course, be very interesting to know the partition of $f(i)$ into cathode and anode parts, but this would require much more extended tests than we have had time to make.

The experimental method for separating the part $f(i)$ of the electromotive force from Ri and e is to cause the current to vary, thus separating Ri and $f(i)$ from e, whence $f(i)$ becomes known when Ri has been determined. The difficulty encountered in the realization of this method is that e is to a certain extent a function of q, because of local changes of concentration of the electrolyte, because of progressive changes in the character of the surface layers of the electrodes, and because of temperature changes due to continued flow of current.

The experimental results which are communicated herewith are based upon measurements made chiefly with an ordinary ammeter and voltameter, so that the changes of current were of necessity comparatively slow. These results, therefore, give values of $f(i)$ which include the slight variations of e, due to concentration changes, etc. Some of the points on our curves, however, have been determined by means of a contact device for giving values of electromotive force within a fraction of a second after the current starts to flow, and we have under way a series of experiments for determining the values of the electromotive force between the electrodes within a hundredth of a second after the current starts to flow and within a hundredth of a second after the cessation of flow of current. These results will be communicated in a subsequent paper.

The method employed by the authors was first used in some very rough measurements carried out by students at Iowa State College in 1895, and of which the results are represented in a figure and shown in the first edition of Nichols and Franklin's Elements of Physics, Vol. II, p. 76. The first experiments making use of rapid changes of current are those described by Professor J. W. Langley,[21] who employed this method to determine the actual value of what we have here called the reversible polarization of an electrolytic cell.

EXPERIMENTAL WORK.

Our plan was to choose an electrolytic cell in which the reversible polarization e is small, so that to a first approximation the measured electromotive force E $(= ri + f(i) + e)$ would be

[12] Trans. Am. Electrochemical Society, Vol. I, p. 255.

equal to ri + f (i), whence the value of the irreversible polarization f (i) is known when *r* and *i* are known.

The electrolytic cell used consisted of a vertical glass cylinder containing two horizontal circular disks of copper, each having an area of 96.05 sq. cm. These disks served as electrodes, and they were held at a distance apart of 0.626 cm. by three small glass cubes. The electrolyte was a copper sulphate solution, specific gravity 1.160 at 18.5° C.; and specific resistance 15.238 ohms per cubic centimeter at 18° C., a slight amount of sulphuric acid being added to increase the conductivity. The temperature of the electrolytic cell during the tests ranged from 16.4° C. to 18.5° C., average temperature being 17.75° C.

The electromotive force across the cell was measured by a Weston laboratory standard voltmeter and the current was measured by a Weston laboratory standard ammeter. Both of these instruments were calibrated during the progress of the work by means of a potentiometer, a standard resistance and a standard cell.

The observations consisted in reading the ammeter and voltmeter at five-second intervals for forty-five seconds after starting the flow of current through the cell, the current being kept constant during each set of readings. The current was then reversed and another set of readings taken. The current was then changed in value, and the double set of readings again taken, and so on. Before each single set of readings the solution was thoroughly stirred. The points on the curves represent the mean of three or four readings.

The values of electromotive force less than five seconds after closing the circuit were determined by a contact device actuated by a plunger moving steadily in an oil dash pot. This plunger carried platinum-tipped wires which made contacts at certain instants by dipping into deep mercury cups. The electromotive force was measured in this case by balancing the electromotive force across the electrolytic cell, at a certain instant, against the "drop" on a slide wire.

The results of our observations are shown by the curves[1] in Fig.

[1] The original drawings from which the two figures were to be made were lost in the mails, and at the last moment new drawings were made. Figure 1 shows one only of the ten or more curves between (E-ri) and time, the various curves being for different values of current; and Fig. 2 shows one only of the eleven or twelve curves between (E-ri) and the current; that is, between approximate values of f (i)

1, in which abscissas represent elapsed times after starting the current and ordinates represent the values of (E — ri), which, as pointed out above, is approximately equal to f (i) for the electrolytic cell we used. The curves shown in Fig. 2 are derived from the curves of Fig. 1, and they show the approximate values of the irreversible polarization [f (i)] as functions of the current. Of course the curve in Fig. 2 corresponding to t = 0 would give the correct values of f (i), but this curve could not be derived from the curves of Fig. 1 for the reason explained below. The curves 1 a and 1 b (Fig. 2) show the nearest approximation obtainable

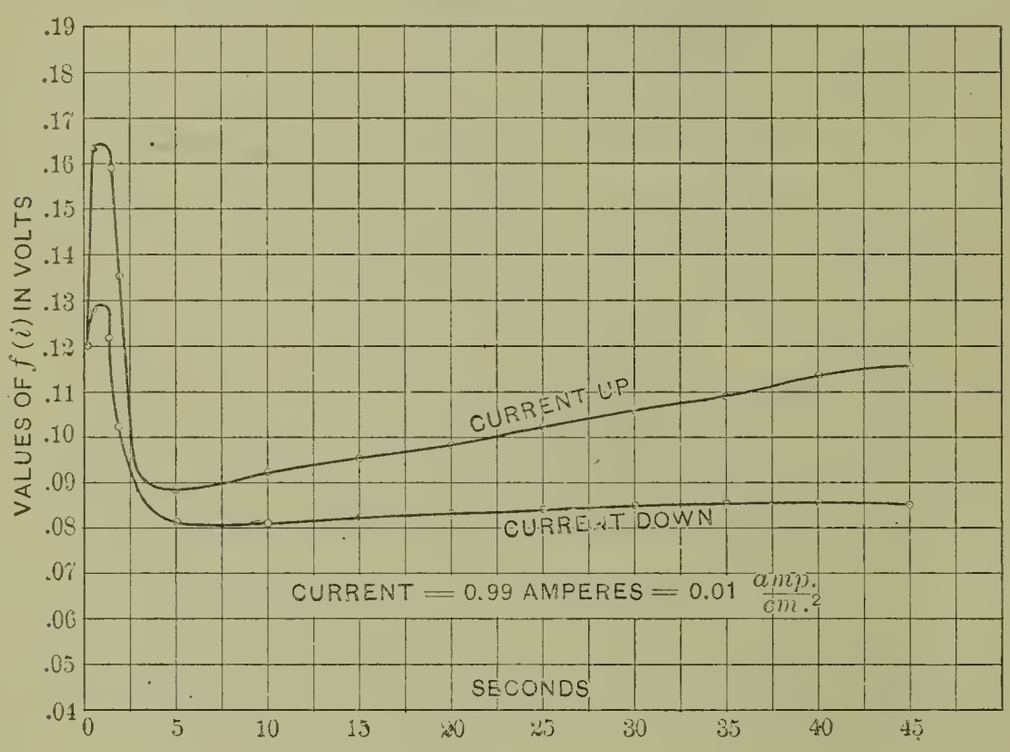


FIG. 1.

from our observations to the values of f (i) for various currents.

The values of f (i) as determined by these measurements involve the values of *c* due to changes of concentration, due to changes in the nature of the surface layers of the electrodes and due to local temperature changes produced by a continued flow of current, and the object in view in determining a curve between electromotive force and time for each value of current was to enable the curve so determined to be extended to t = 0 (the instant at which the current starts to flow),

and i. The curve given in Fig. 2 is the nearest approach of all the curves of this set to the ideal curve between f (i) and i, when t = 0; that is, without lapse of time after starting current flow before observing electromotive force values.

thus giving some indication of the value of f (i) unaffected by reversible polarization. This method of exterpolation to t = o proves to be very unsatisfactory with the observations we have made because of the singularity of the electromotive—force—time curves near t = o, as shown in Fig. 1. This singularity seems to be due to rapid changes in the nature of the surface layers of the electrodes, inasmuch as this singularity seems to be absent in some recent observations in which the current is not reversed before each set.

The very considerable degree to which values of reversible

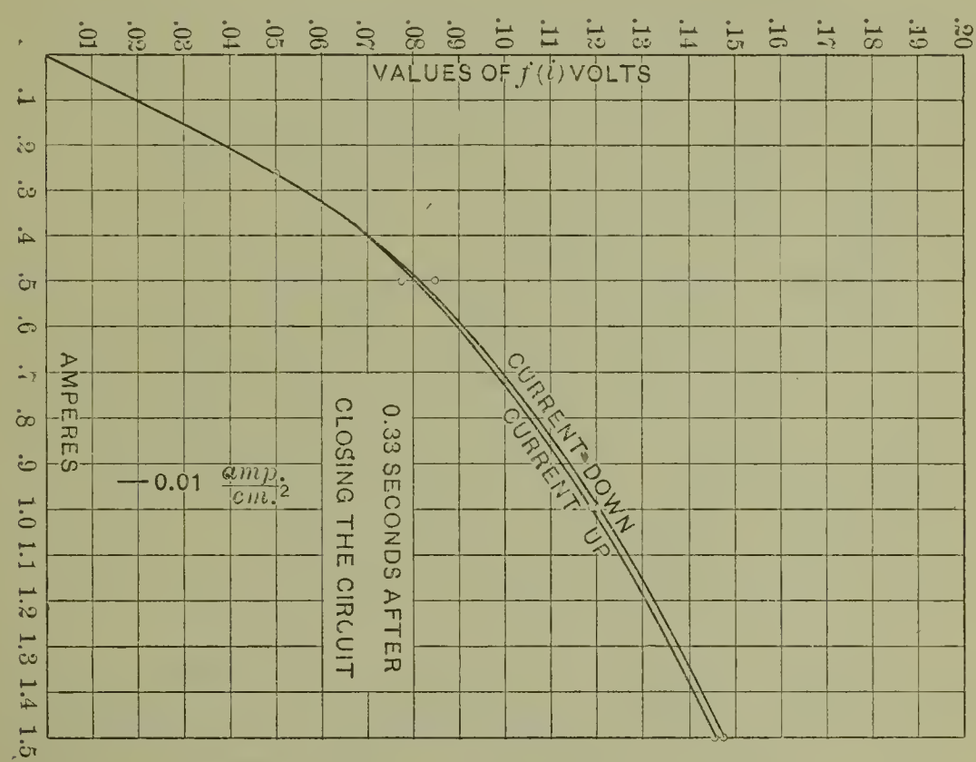


FIG 2

polarization [e] enters into the observed values of E — ri, which are plotted in Fig. 1 as approximate values of f (i), may be seen by the difference between the ordinates of the curves for up-flowing current in the electrolytic cell and the curves for down-flowing current in the cell. In fact the values of E — ri are uniformly greater when the current flows up than when it flows down. When the current flows down the solution becomes concentrated at the upper plate and more dilute at the lower plate, hence convection of the liquid assists diffusion. When the current flows up the lighter solution is at the top, and diffusion alone operates to equalize concentration. As the elapsed time becomes smaller the

values of E — ri for up- and for down-flowing current become more nearly equal. This is consistent with the idea that E — ri becomes equal to f (i) at t = o, and of course f (i) is sensibly independent of gravity.

The values of *ri* were nearly one-half of the total measured electromotive force E between the electrodes, and therefore every care was taken to determine the correct value of the resistance *r* of the electrolyte between the electrodes. The specific resistance of the copper sulphate solution was measured by means of a Kohlrausch bridge in terms of a standard solution of 30¼ per cent. of H_2SO_4. The value of *r* calculated from this result was checked by measuring the electromotive forces between the electrodes with constant current and with different distances between the electrodes. The value of *r* so determined agreed within 2 per cent. with the value calculated from the specific resistance as determined by the Kohlrausch bridge.

The resistance between the copper plates was also measured directly with the Kohlrausch bridge. This gave results from 5 to 10 per cent. too high. This was to be expected, as the irreversible polarization at copper electrodes in a copper sulphate solution is by no means negligible. In this connection it may be well to state that irreversible polarization effects cannot be satisfactorily expressed in terms of an electrode or transition resistance. There is for a certain current a certain rate of dissipation of energy $\Phi(i)$ at the electrodes of a given cell, and this dissipation of energy is associated with a definite measurable back electromotive force, $\Phi^{(i)}/_i$ or f (i), but it is confusing to divide this rate of dissipation of energy by i^2 and call the result a resistance.

DISCUSSION.

Mr. Carl Hering: I have not been able to follow Dr. Franklin entirely in his paper, as he uses terms which are somewhat different, in some respects, from those that we are accustomed to. Polarization is one of those terms which seem to have a very indefinite meaning. Definitions taken from various standard works differ very appreciably. Different writers use it for radi-

cally different quantities. As Dr. Franklin says, the phenomena in electrolysis are very complex, and it is therefore difficult to separate them entirely; but when we talk about polarization it seems to me we ought to all use the term in the same sense. If, for instance, we electrolyze copper sulphate between vertical copper electrodes and small current density, we know there is no polarization; yet if we place those plates horizontally and make the cathode the upper one, we soon find, if we look through the blue liquid horizontally, that there is a layer of what looks like water immediately below the cathode. That means that all the copper sulphate has been exhausted from that layer which is immediately in contact with the cathode. A voltmeter put in circuit would then show, according to Dr. Franklin's paper, that there would be polarization; there would then be hydrogen evolved, because there is no longer any copper sulphate next to the cathode, and the only thing that can separate out is hydrogen. Some would call this polarization. Now is that really polarization, or not? That phenomenon takes place in a great many cases in which the layer immediately next the cathode becomes exhausted of the thing that we think we are electrolyzing; hence we are electrolyzing something else. Now that layer may be only as deep as a molecule, and therefore entirely invisible; and yet the results produced would not be those which we expect, and the question is, is that polarization?

Platinum, which is the metal that is most frequently used in such experiments (although in my opinion the worst one to use), has a very peculiar property of absorbing oxygen and hydrogen; in fact, it has a very strong tendency to absorb them, so strong that if we take a piece of spongy platinum and blow a stream of hydrogen against it, it gets red-hot, as is well known, because it has absorbed gases to such an extent; hence electrodes made with platinum would be most likely to give entirely incorrect quantitative results. The energy of this affinity for gases appears in the voltage during electrolysis, and this, in my opinion, is the reason why there is such discrepancy in researches with the electrolysis of water.

I do not think Professor Franklin separates out very clearly the voltage of decomposition, which is sometimes reversible and sometimes irreversible. If we decompose water (or strictly

speaking sulphuric acid) we get oxygen and hydrogen which escapes; whereas if we decompose something which remains on the plates, these plates may act as a battery and give that energy back when we reverse the current. Therefore the voltage of decomposition is sometimes reversible and sometimes not.

There is also present what seems to be a thermoelectric action. We know from Caspari's results that it takes a greater voltage to separate out hydrogen gas from a cathode of zinc, for instance, or mercury, than it does from one of platinum. It is different for zinc than for mercury; both, again, are different from the voltage required for silver, and the question is, what is the seat of this extra electromotive force? It seems to me it can only be thermoelectric; and of course it is then not reversible. If it is thermal, it is like sending a current through a thermoelectric junction of two metals.

In the electrolysis of water (or strictly speaking sulphuric acid), it seems to me there are two things which we do. In the first place, we are separating oxygen from hydrogen, we are severing the chemical bond between them. The energy for doing this unquestionably comes from the current. Then there is a second phenomenon, which is, that those gases expand to about 1600 times their former volume (I think that is the figure); in other words the gases, after the electrolysis, have about 1600 times the volume they had before, when they were water or acid; hence, work has been done in expanding these gases to that very great volume against the atmospheric pressure. The question therefore arises, does this energy come from the electric current, or not? It seems to me that it cannot come from the electric current; it seems to me that it must come from the abstraction of heat from the liquid. If it does not come from the electric current, and if it gives back energy when we reverse the current for an instant, can we call it polarization, or not? If we call this factor of the energy polarization, and if that energy is purely thermal, it leads us to the absurdity that this kind of polarization gives back energy which did not come from the original current at all.

I mention all this merely to show how carefully we should use this term polarization, and the great importance of defining clearly what we mean. Professor Franklin, as I understand it, says that anything not accounted for by the I^2R loss, is polarization. This

certainly has the advantage of simplicity, and is a sure way of balancing a purely mathematical equation, but unfortunately it does not help us in the least to understand what is going on, as this single quantity is really a very complexed one made up of a large number of factors which may be radically different from each other, and some one of which, like the thermoelectric effects, ought surely not be included under polarization.

PROF. FRANKLIN: I am rather surprised that Mr. Hering does not see a precise and legitimate definition of polarization in the paper. It seems to me that the only kind of a definition which is good for anything is one which can be used as a basis for measurement. The conception that we may have of electrolytic polarization is a very different thing from the mathematical definition of it which lies at the basis of our methods of quantitative work.

If a certain electromotive force acts upon a cell, or if we expend work on the cell, the question is, in what different ways is this work used? In the paper this work is separated into three definite parts. One part of this work appears only in the electrolyte, in accordance with Joule's law. The work so spent may be separated experimentally from the work spent in every other way; because if you like you can make an electrolytic cell a mile long and you can make measurements all along the line, whereas the energy liberated at the electrodes would be local and could be experimentally separated from the other. This first part of the work, then, is certainly experimentally distinct.

Now in the second place we all know that there is work that appears as heat at the electrodes. This is the case even in the electrolysis of sulphate of copper between copper electrodes. The experimental work that I intend, with your permission, to show you to-morrow, has been wholly carried out on just such electrolytic cells (sulphate of copper between copper electrodes); and this irreversible expenditure of energy at the electrodes, that is, the product of current into the irreversible electromotive force of polarization, does exist in such cells according to our results.

In the third place, as to the work involved in item (c), the work which is used to supply the energy which is represented by the chemical change, we all know that there is a necessity for the doing of that work; because after the passage of a certain

charge through the cell the total energy of the system is different from what it was before.

The precise ideas of polarization depend upon a clear distinction between the two terms (b) and (c). I define polarization simply as that part of the back electrolytic force of the cell which does not include *ri*. That defines polarization as a measurable quantity. Now this total polarization can, it seems to me, be separated mathematically into two distinct parts, and the definitions of these two parts as given in the paper serve as a basis for the devising of experimental methods to separate them in reality. Of course, we know that the total back electromotive force of an electrolytic cell, aside from that part due to resistance, depends on the current and also upon the amount of charge which has passed through the cell; because all concentration changes, all local temperature changes, and all changes in the nature of the surfaces of the electrode are functions of the time integral of the current. All these sources of electromotive force depend upon the configuration of the system, the chemical and physical configuration, and all those electromotive forces are strictly reversible from a thermodynamic point of view; because the reacting force in the system depending only on the configuration, if you change the velocity of the system from one direction to the reverse, the force of reaction will always give you back the same amount of energy that you put in. However, the reversible effects which contribute to the existence of the reversible polarization may depend upon the maintenance of a certain mechanical configuration of the system; that is, upon the keeping of the products of decomposition available for the reverse reaction; and the fact that they become non-available is due to thermodynamically irreversible processes which are subsequent to and independent of the electrolytic process. Thus the collection of hydrogen as bubbles and its escape is an irreversible process which is independent of the fundamental processes of electrolysis themselves. It seems to me that we will be able to separate the various activities that take place in an electrolytic cell into those which are fundamentally associated with the electrolytic process and those which are subsequent to it and independent of it.

The irreversible part of polarization is that which is a function of the current, not a function of the configuration of the system;

understanding that by the word configuration we include all of those changes in the cell due to the passage of a charge through the cell as well as to the mechanical displacements of the constituents of the cell. It seems to me that the definition of polarization in terms of measurable quantities in a way which may lead to give precise results is a very different matter from the conception of polarization as a physical action.

Nernst's idea of solution tension of the ions of a metal is a very good basis for a conception of reversible polarization, and if irreversible polarization, f (i), is found to exist we may get a picture of it in this way: In order that ions may be deposited at a finite rate on an electrode it may be that a certain degree of supersaturation of the ions in the layer of electrolyte near the electrode is necessary, so that ions are dragged up into this supersaturated region from which they fall down, as it were, on the electrode. If the current be reversed, however, the ions may not go into solution off the electrode at a finite rate unless the layer of electrolyte near the electrode is undersaturated, so that the ions fall down, as it were, from the electrode into the solution, whence they are dragged up by the electromotive force into the portion of the solution remote from the electrode.

A paper read at the Seventh General Meeting of the American Electrochemical Society, held at Boston, Mass., April 25, 1905. President Carhart in the chair.

NOTES ON ECONOMIC TEMPERATURES OF COPPER-REFINING SOLUTIONS.

By Charles F. Burgess.

The temperature co-efficient of metallic conductivity is an important factor which enters into the calculations of the electrical engineer in his design of electrical conductors and apparatus. The temperature co-efficient of electrolytic conductivity, on account of its much greater magnitude, is a factor of correspondingly greater importance to the electrochemist. Unfortunately, however, the constants in the latter case are much more uncertain, and have not been worked out to the degree of accuracy as have metallic conductors.

That the electrochemist is dependent more upon experimental trial than upon well-known data in the determination of his constants is demonstrated in the admirable paper presented by Dr. Bancroft before this Society on "Electrolytic Copper Refining." (Vol. IV, Transactions). This paper contains various suggestions relative to the economical refining of copper, an important one of which is that greater economy can be effected if the solutions are run at a higher temperature than has been commonly adopted by the refineries.

The pressure between the two electrodes of a copper-refining tank is the sum of two quantities, the polarization pressure and the drop caused by the current flowing through the electrolyte. The former is small and may be considered as practically constant for a given solution, being influenced very slightly by the temperature. The IR drop through the electrolyte varies, however, in a marked degree with change of temperature, and it is this variation which causes the falling off in applied pressure necessary to pass a given current through the cell as the temperature rises.

Abstracts from the data given in the paper above referred to show that with copper electrodes one centimeter apart, in a solution containing 16 per cent. copper sulphate crystals and 9 per cent. free acid, and with a current of 3.5 ampères per square decimeter, the pressure at the electrode terminals is, for various temperatures, as given in Table I.

TABLE I.

Temp.	Voltage at Electrode Terminals	In Terms of Voltage at 20°
20°	.354	100
30	.298	84.2
40	.248	70
56	.217	61.3
60	.188	53
70	.165	46.6
80	.142	40
90	.129	36.4

From these figures it appears that the pressure at 70 degrees is less than half that required at 20 degrees for the same current, and consequently that the cost for power is less than one-half. It is stated that "by expressing voltage in terms of the voltage at 20 degrees," as is done in column 3, "the effect of the distance between the plates is eliminated," and that "the percentage variations hold for any set of plates in the same solution."

This assumption, which served as a basis upon which various conclusions were drawn, would undoubtedly be correct if we are concerned only with the specific resistance of the electrolyte itself, but since it is the virtual resistance between the electrodes that is involved, the assumption is not justified.

The resistance of the cell includes the resistance between the electrode surfaces and the electrolyte, and the resistance of the electrolyte itself. The former is of considerable magnitude in comparison with the latter when the electrodes are close together, and of much less relative magnitude when a considerable column of electrolyte intervenes. The temperature co-efficient at the electrode surface resistance is much greater than the temperature co-efficient of the electrolyte, and unless these separate resistances and their corresponding temperature co-efficients be known, it is impossible to calculate the temperature co-efficient of the complete cell with electrodes five centimeters apart from measurements on electrodes one centimeter apart.

The following experiments bearing on this point were performed: A solution consisting of 160 g. $CuSO_4$ $5H_2O$ and 90 g. H_2SO_4 per liter was employed. Two copper plate electrodes, 2 inches wide, completely occupied the cross-section of a rectangular glass vessel, 2 inches x 5 inches x 5 inches deep. Electrodes were first placed 4½ inches apart, with the electrolyte 2¼ inches deep, and a current of about one ampère applied. The glass trough was heated by means of a water bath and, with constant stirring, the temperature was gradually raised. A similar run was made with the electrodes placed about ⅜ inch apart. The observations are given in the following tables. Measurements of current and pressure were made with Weston portable instruments recently calibrated.

TABLE II.

With electrodes 4½ inches apart.

Temp.	Voltage at Electrodes.	In Terms of Voltage at 20°
20°	1.57	100
23.5	1.5	95.5
31	1.35	86
41	1.22	77.7
49	1.17	74.5
60	1.1	70
67	1.07	68

TABLE III.

With electrodes ⅜ inch apart.

Temp.	Voltage at Electrode Terminals.	In Terms of Voltage at 20°
20°	.36	100
24	.32	89
30	.27	75
38	.22	58
46	.18	50
52	.16	44.5
60	.14	38.9
67	.13	36

The counter e.m.f. taken upon interrupting the current was constant at about .025 volt.

The tables II and III, and corresponding curves, Fig. 1, show clearly that the lowering of voltage is not proportional to the increase of temperature regardless of the distance between the plates, but that on the other hand the temperature effect is far more marked when the electrodes are close together than when

they are far apart. In other words, the apparent temperature co-efficient is dependent upon the distance between electrodes, being greatest when the electrodes are close together.

We are not, therefore, warranted in saying that the most economical temperature in a cell with the plates one centimeter apart is the most economical for a cell with the plates ½ inch or 1½ inches apart, as in the series and multiple refining systems respectively.

An explanation for this marked variation in temperature co-efficient with various distances between electrodes is afforded in that phenomenon which Gore chose to call "transfer resistance." "Transfer resistance," as defined by him (*Phil. Mag.* V. 21, 1886, p. 130), is "a species of electric resistance distinct from that of

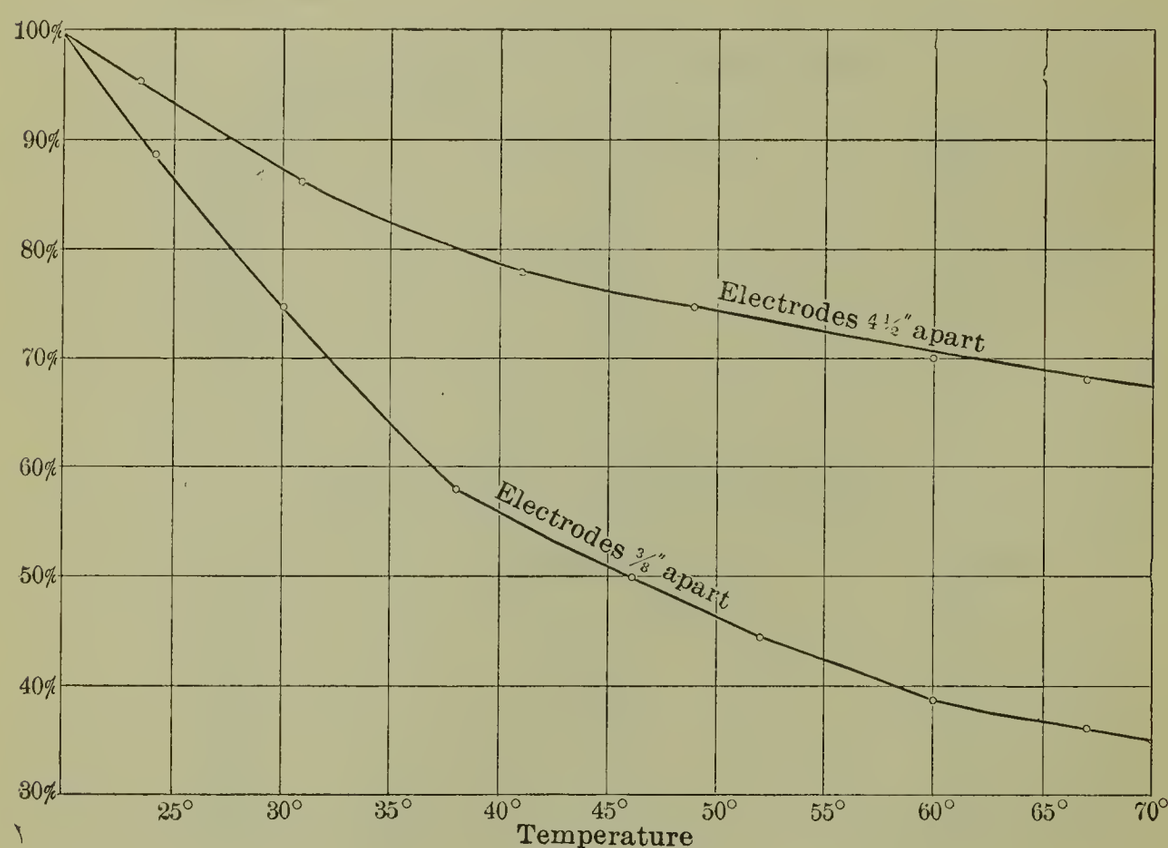


Fig. 1

polarization and ordinary conductive resistance, varying greatly in amount in different cases, which exists at the surfaces of mutual contact of metals and liquids in electrolytic and voltaic cells," and "this resistance varies largely in amount with different metals in the same solution, and with the same metal in different solutions." Gore measured the effect of this "transfer resistance"

by means of the heating effect on the air inclosed in a thin platinum electrode, as well as by other means described in later papers published in the same volume of the *Philosophical Magazine.*

A distinction is made between the term "transfer resistance" and "surface resistance," the latter including the changes in the electrolyte produced by electrolysis. It was found that in general this resistance is greater at the cathode than at the anode, and that by increase of temperature the transfer resistance is usually and considerably reduced. In a short-circuited cell, using a platinum cathode and zinc anode, he states that raising the temperature from 14 degrees to 95 degrees increased the e.m.f. by 8.38 per cent., while the amount of current flowing was 220 per cent. greater, this being due largely to the decrease of the "surface resistance."

If there exists, therefore, a resistance at the electrode surface apart from the resistance of the electrolyte itself, of such nature that it has a great temperature co-efficient, we have an explanation of the dependence of the apparent temperature co-efficient of an electrolyte upon the distance between the electrodes, the reduction of the "transfer resistance" producing a greater proportion of the total change when the electrodes are close together than when farther separated.

To obtain additional and more accurate data upon this phenomenon, a rectangular slate tank, of the dimensions 2½ inches x 6 inches x 6 inches deep, was fitted with copper electrodes, one set being accurately spaced at ⅜ of an inch apart, and another set at 1½ inches. The electrodes fitted so closely in the cell that only one side of each plate was active as an electrode surface. The solution used was a 16 per cent. $CuSO_4$ $5H_2O$ and 9 per cent. H_2SO_4. The tank was heated over a sand bath, the electrolyte being stirred to maintain uniformity and avoid concentration effects.

In Table IV are given data showing the effect of increase of temperature on the resistance. The columns marked "apparent specific resistance" give the resistance per cubic inch as calculated from the current and applied pressure; those marked "corrected specific resistance" give the values obtained by deducting the polarization pressure, which was determined by the voltmeter

immediately after interrupting the current. The electrolyte was not heated beyond 56° C, on account of the failure of the cement of the tank to stand a higher temperature. The current of one ampère had a density of 20.8 ampères per square foot.

TABLE IV.

Electrodes ⅜″ apart.			Electrodes 1½″ apart.	
Apparent Sp. Res.	Corrected Sp. Res.	Temp.	Apparent Sp. Res.	Corrected Sp. Res.
3.95 ohms	3.74 ohms	29° C	2.16 ohms	2.105 ohms
3.12 "	2.91 "	40 C	1.85 "	1.79 "
2.70 "	2.50 "	50 C	1.64 "	1.59 "
2.50 "	2.29 "	56 C	1.56 "	1.51 "

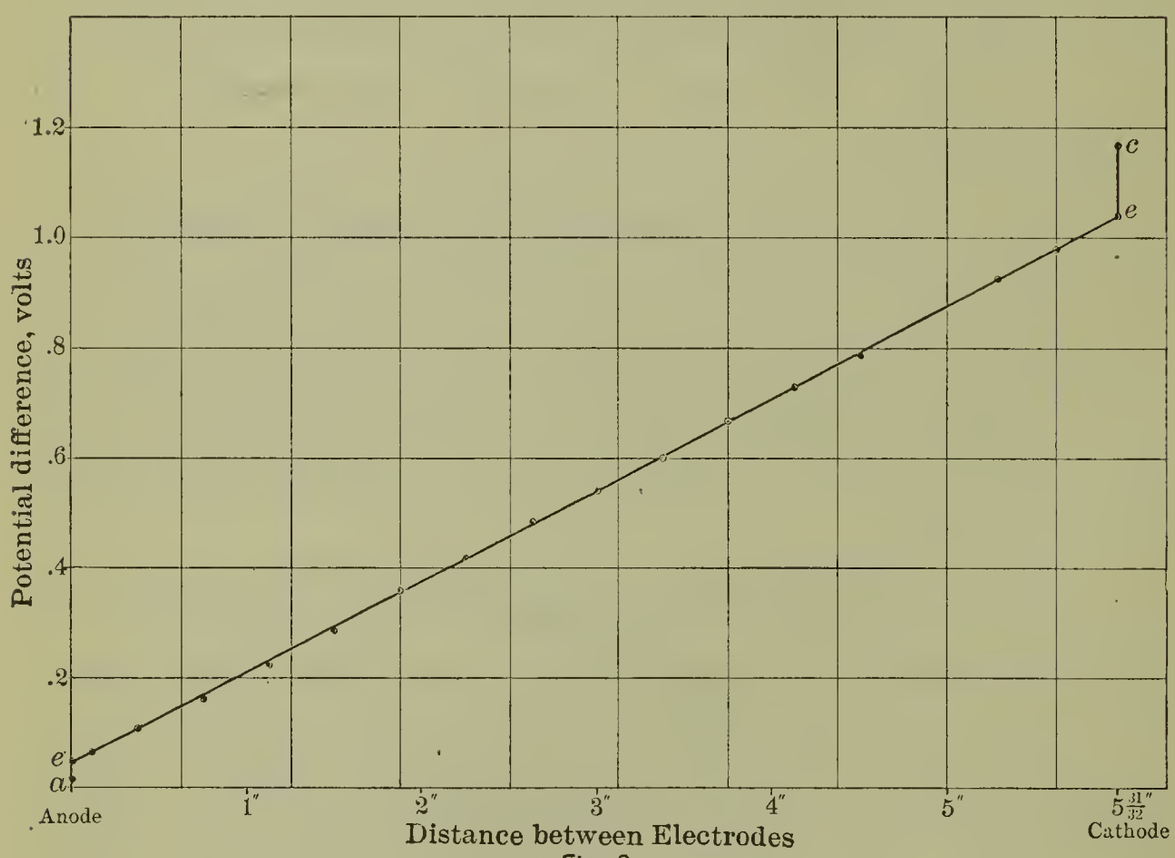


Fig. 2

It is to be noted that while the specific resistance with the plates close together decreased 36.7 per cent. for an increase of temperature of 27 degrees, the specific resistance with the plates farther apart decreased only 27.7 per cent.

To determine what influence the free acid might have on this variation of specific resistance, a run similar to the preceding was made, using a neutral solution of 16 per cent. copper sulphate crystals. Table V gives the results of this run.

TABLE V.

Electrodes ⅜″ apart.			Electrodes 1½″ apart.	
Apparent Sp. Res.	Corrected Sp. Res.	Temp.	Apparent Sp. Res.	Corrected Sp. Res.
11.85 ohms	11.73 ohms	32° C	11.00 ohms	10.97 ohms
11.45 "	11.30 "	37 C	9.97 "	9.95 "
10.82 "	10.67 "	40 C	9.60 "	9.57 "
9.96 "	9.86 "	46 C	9.20 "	9.17 "
9.55 "	9.48 "	50 C	8.73 "	8.72 "
9.35 "	9.30 "	52 C	8.63 "	8.60 "

The specific resistance is seen to decrease 21 per cent. with electrodes ⅜ inch apart, and 21.5 per cent. with the electrodes spaced 1½ inches. From this it may be concluded that the change of resistance with temperature is due almost entirely to temperature co-efficient of the electrolyte itself, and not partially to electrode effects, as is the case when the solution is acidulated.

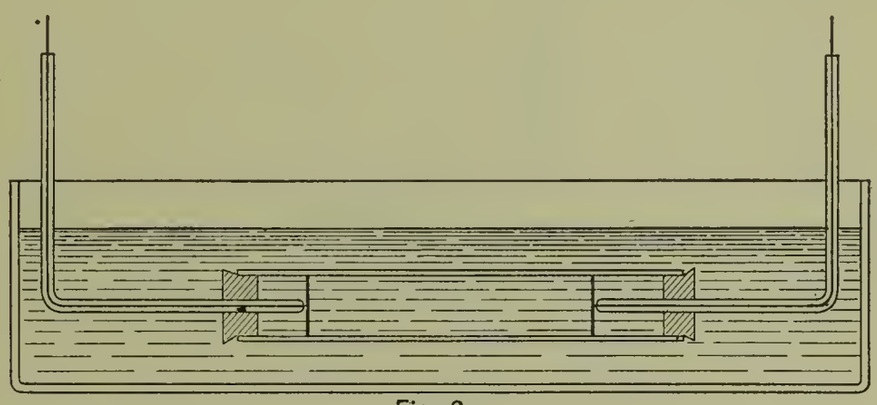


Fig. 3

A further analysis of the electrode effect was made by tracing the fall of potential from the anode to the cathode. This was done by means of the normal "calomel" electrode, the liquid terminal of which consisted of a glass rod drawn to a fine point and bent in such a way that it could be placed in contact with the electrode, and then moved step by step measured distances toward the other electrode. The potential differences between the normal electrode and the copper electrode were measured by the well-known potentiometer method.

The data relating to this test are given in Table VI, and the results plotted in Fig. 3.

TABLE VI.

Current p 1 amp. = 18.9 amp. per sq. ft.
Distance between electrodes = 5-31/32″.
Solution: 160g. $cuSO_4$ $5H_2O$ and 90g. H_2SO_4 per liter.

Temperature = 22° C.
Measurement of fall of potential made by means of glass rod terminal of calomel electrode drawn to a fine point and placed at various distances from the electrodes.

Distance of normal electrodes terminal from anode.	Volts.	
0	.0106	=anode polarization.
0	.0424	=potential between electrode and solution.
1/8″	.0635	
3/8	.106	
3/4	.163	
1-1/8	.222	
1-1/2	.286	
1-7/8	.354	
2-1/4	.413	
2-5/8	.477	
3	.536	
3-3/8	.600	
3-3/4	.664	
4-1/8	.725	
4 1/2	.787	
4 7/8	.850	
5 1/4	.916	
5 5/8	.980	
5-31/32	1.037	
5-31/32	1.176	= potential between anode and cathode.

Total polarization as measured by voltmeter = 0.2 volt.
Cathode polarization = .0106. Anode polarization = .0094.
Specific resistance, eliminating electrode effect = 1.26 ohms per cubic inch.
Specific resistance, as calculated from current and applied pressure = 1.5 ohms.
Specific resistance, as calculated from current and applied pressure, with electrodes 1-1/2″ apart = 2.12 ohms.
Specific resistance, with electrodes 3/8″ apart = 4.67 ohms.
Specific resistance, with electrodes 1/8″ apart = 11.46 ohms.

It is to be noted that the fall of potential through the electrolyte is represented by a straight line, which is to be expected if a solution of constant composition be maintained by suitable stirring. The polarization, as measured by the voltmeter upon interruption of the current, was .02 volt, apportioned nearly equally to the two electrodes. There is a resistance effect at the surface of the copper electrodes, causing a fall of potential much more marked than the polarization effect. This surface resistance appears to be considerably greater at the cathode than at the anode, as shown graphically by the vertical lines *ec* and *ae*, respectively.

It might be urged that this marked drop of potential at the electrode surfaces is due only to polarization, and that the method of measuring polarization by opening the circuit gives only a portion of the total value. This is hardly possible, however, since

a polarization of about .2 volt would have to be assumed, which is apparently out of the question.

Neither does it appear to be due to changes of composition of the solution as a result of electrolysis, since in this case the effect would be materially decreased by agitation of the electrolyte. In making the measurement it was noted that the agitation of the solution had very little influence on this surface resistance.

The question arises as to whether this surface resistance is an inherent mutual property of the metal and the solution, or whether it is produced as a result of the flow of current. It is apparent that the flow of current has some influence on the amount of the resistance, as shown by the fact that it is different at the two electrodes when a direct current flows. Mr. O. P. Watts has given me permission to quote from his laboratory notes some data bearing upon this point.

A glass tube, as shown in Fig. 3, was filled with a copper sulphate solution containing 100 grammes of the crystals and 100 grammes of sulphuric acid to the liter. Copper disc electrodes closely fitting in the tube were adjusted by means of a glass tube passing through the rubber stopper at either end of the tube. The specific resistance of the electrolyte maintained at 23° C, by immersion in a constant temperature bath, was determined first by means of an ampèremeter and a voltmeter, using a current density of 4.2 ampères per square decimeter, and then by the Wheatstone bridge method, using an induction coil as the source of current and the telephone receiver as the detector. In Table III, column 2, is given the apparent resistance per cubic centimeter by means of the fall of potential method, and in column 3 similar values by the bridge method.

TABLE VII.

Distance between Electrodes.	Ohms per c. c. By Ammeter and Voltmeter.	Ohms per c. c. By Wheatstone Bridge.
20	2.02	1.84
18	1.95	1.79
16	2.04	1.81
14	2.01	1.82
12	2.08	1.83
10	2.09	1.88
8	2.26	1.81
6	2.38	1.95
4	2.74	2.03
3	3.17	2.19
2	3.81	2.43
1	6.19	3.24

The apparent specific resistance with the electrodes one centimeter apart is about three times as great as the true specific resistance when the direct current is flowing, and when the very small alternating current, the distance is not so great, though it is still quite marked. This shows, therefore, that the electrode effect is not a result of electrolytic products, since it also accompanies the flow of alternating current of such small value as to make the accumulation of electrolyte products impossible.

Laboratory of Applied Electrochemistry,
University of Wisconsin.

DISCUSSION.

PRESIDENT CARHART: Mr. Burgess' paper is open for discussion. I am sorry Professor Burgess is not here to discuss it.

PROF. W. S. FRANKLINS I am surprised to hear the author set aside, as being out of the question, the existence of as much as 0.2 volt of polarization in the neighborhood of a copper electrode. The results of Mr. Freudenberger and myself, as found with copper electrodes, show the existence of polarizations running up to 0.1 volt with current densities which, I take it, were much smaller than those which Professor Burgess used. The table given by Professor Burgess on page 58 is a table of observed electromotive forces which can be separated into two distinct parts, one of which is proportional to the distance between the electrodes, namely, the *ri* part, and the other is constant in value. It is upon a set of observations exactly like this that Mr. Freudenberger and I separated the reversible and the irreversible polarization.

F. A. LIDBURY: Did you find the polarization in the case of copper to exist in the cathode or in the anode?

PROF. FRANKLIN: We made no attempt to separate the polarization into cathode or anode parts. Our first object was to show the existence of both a reversible and an irreversible polarization without regard to its seat at one electrode or the other.

MR. LIDBURY: According to Professor Burgess' paper, on page 56, the resistance is at the cathode.

MR. CARL HERING: Quite a number of years ago I made some tests with a standard Daniell's cell, and found that the electromotive force was quite appreciably influenced by differences of pressures on the two liquids. On the test described on page 58, it seems to me that such pressures might cause quite appreciable differences in the results, because, as I understand the experiment, the tube was sealed with two corks, and a slight amount of gas liberated in the tube would create a different pressure, and that might affect the result quite appreciably.

DR. M. DE K. THOMPSON: On page 53 Professor Burgess gives the measurement of the counter-electromotive force in this cell, and finds it to be only .025 volt; and I suppose it is from that observation he states that the .2 volt is out of the question. I suppose he had a concentrated solution of copper sulphate in the experiment on page 58. No gas would be liberated in that case, and there would be no change in the pressure.

MR. HERING: I am well aware of the fact that there *ought* not to be gasing; but I am also aware of the fact that there very often is gasing, and when the tube is sealed there will be a pressure produced. As soon as the copper sulphate has been exhausted even from only a molecularly thin layer next to the cathode, there will be sulphuric acid next to the cathode, and there will be gases formed, even though invisible in amount.

PROF. FRANKLIN: The electromotive forces he says were .025 volt, according to the statement, on interrupting the current; the reversible polarization, however, exists only while the current is flowing, and it vanishes when the current ceases to flow.

PRESIDENT CARHART: Irreversible or reversible?

PROF. FRANKLIN: The irreversible polarization exists while the current is flowing; it is this that I had in mind in connection with the 0.1 volt.

DISCUSSION.

(*Communicated by Lawrence Addicks previous to the meeting.*)

Prof. Burgess presents a series of data very interesting to me, but I am sorry he does not attempt to answer the conundrum. There can be no question that a transfer resistance of considerable

magnitude exists in copper refining work, and that it is ohmic in its nature. Polarization effects can easily be separated by measuring the voltage at different current densities with a constant temperature. The voltage for zero current density can then be found by extrapolation. A common figure for polarization in an actual copper refining cell is 0.02 volt.

For some time I have been inclined to think the explanation of transfer resistance is connected with the presence of gases near the electrodes. The specific resistance to be dealt with must be very high, as the effect is entirely within a layer of exceedingly small thickness, but free gas, at least, would have practically no conductivity. The cathode effect is greater than the anode, but the hydrogen naturally at the cathode has half the valence and therefore twice the volume of the oxygen near the anode. On the one hand, the temperature co-efficient of this layer is enormous, and on the other, both the solubility of gases in liquids and the volume of free gas are greatly affected by temperature. The effect becomes small at high temperatures, and in a boiling solution there could be no gas effects. The parallel seems to me at least suggestive.

The amount of transfer resistance also seems to be closely connected with the acidity of the electrolyte, as the results in the paper indicate. Laboratory results on the specific resistance of electrolytes indicate that there would be money in carrying the free acid in the electrolyte to over 20 per cent., but in practice about 13 or 14 per cent. is found to be the economic limit, even with unlimited circulation to overcome the polarization tendency of the higher acid electrolyte. While I have never directly determined the cause of this apparent discrepancy, it is doubtless due to increased transfer resistance.

A paper read at the Seventh General Meeting of the American Electrochemical Society, held at Boston, Mass., April 25, 1905. President Carhart in the chair.

A DIAPHRAGM CELL FOR ELECTROLYSIS OF SODIUM CHLORID SOLUTIONS.

By Clinton Paul Townsend.

The electrolysis of sodium chlorid solutions with insoluble anodes under conditions which permit the liberated sodium to decompose water may readily become a complex operation by reason of the variety of secondary products which may result. If it be desired to isolate with substantial completeness the chlorin, which is the primary anode product, from the sodium hydroxid, which is the secondary cathode product, it is necessary, first, to prevent the mechanical mingling of anode and cathode solutions, and second, to prevent the sodium hydroxid formed at the cathode from participating in the electrolysis. The first of these conditions is readily secured by a variety of means, but the second has heretofore proven impossible of complete accomplishment.

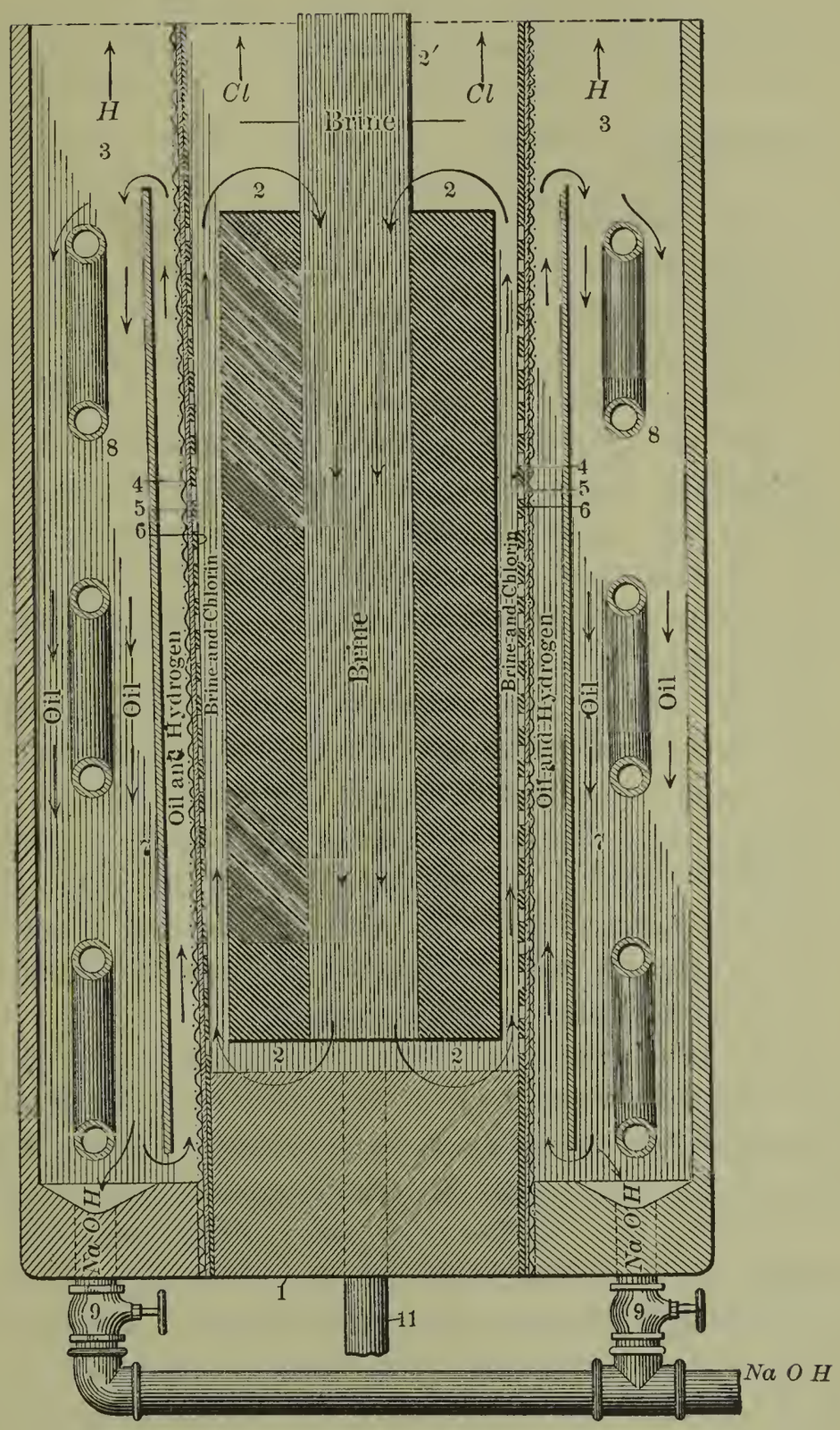
As regards the mixing of the solutions, both anolyte and catholyte are necessarily in more or less violent motion due to gas evolution. It is evident, however, that any device or disposition of parts which will insure a quiescent region of contact between these solutions will avoid their mixing. This is easily accomplished in the various gravity cells by depending partial partitions or bells which provide a quiet lower stratum of electrolyte. It is as readily accomplished by a diaphragm, say of thin asbestos paper, the interstices of which provide the necessary quiescent layer.

A diaphragm of this character does not for practical purposes check the movement of the caustic by diffusion into the anode chamber, or the migration of the hydroxyl ions toward the anode if the conditions be such that the hydroxid takes part in the electrolysis. The diaphragm cell and the gravity cell may therefore be expected to work at ampère efficiencies of the same general order, and the published data seem to bear out this conclusion.

This ampère efficiency is understood to lie in practice between 75 and 85 per cent. These figures represent current losses which are in themselves serious; the losses are doubly serious in practice because they are largely represented by hypochlorite and chlorate in the anode liquor, in the presence of which graphite anodes rapidly disintegrate, yielding an impalpable carbon dust which will soon put a diaphragm cell out of commission. The use of platinum anodes is a possible alternative, but a costly one for cells equipped at the present time, and moreover they do not reduce the power losses. This latter objection holds against the practice of decomposing the hypochlorite in the anode compartment by addition of hydrochloric acid.

The statement is frequently made that if the rate of flow toward the cathode be rapid enough to compensate the migration velocity of the hydroxyl ion the ampère efficiency should be 100 per cent. This proposition applies to gravity and diaphragm cells alike, and is the basis of some of the earliest forms. As a matter of fact, however, the solution which flows from anode to cathode carries a very considerable percentage of dissolved chlorin, and practical experience has shown that, long before such rate of flow has been reached that hypochlorite and chlorate disappear from the region of the anode, the losses by the action of this chlorin on the cathode products become serious. Under such extreme conditions that the moving liquid can dissolve all of the chlorin the caustic efficiency of the cell will fall to zero.

The instantaneous removal of the caustic as formed from the electrolytic field and from contact with the anode liquor would mean the avoidance of all difficulties which arise from the presence of hydroxyl ions in the anode compartment. The chlorinated liquor would then remain free from hypochlorite or chlorate, graphite anodes should be substantially permanent, and the evolved chlorin should be pure. This result is nearly and perhaps fully accomplished by a cell the lower portion of which is somewhat diagrammatically illustrated herewith in transverse vertical section. The experimental cell has a central or brine compartment (1), having cement walls and carrying spaced anodes (2), (2). These anodes, as well as their conductors (2^1), are of Acheson graphite. The lateral compartments 3, 3, are of iron, and in operation are


H
3
Cl
2′
Brine
2
8
4
5
6
Oil
Oil and Hydrogen
Brine and Chlorin
Na O H
9
1
11

filled with a mineral oil which completely submerges one face—the back—of the wire net cathode (4). The active face of this cathode is in contact with the diaphragm (5), which is, of course, quite permeable to the chlorinated anode liquor. The diaphragm is supported on the side toward the anode by a pervious layer (6) of good mechanical strength; 7, 7 are steel plates adjacent and parallel to the cathodes and submerged in the oil; 8 are pipes for maintaining the temperature of the oil and thereby of the electrolyte; 9, 10 is the caustic outflow, and 11 the brine inlet.

The chlorin liberated at the anode faces rises through the narrow channels between the anodes and the diaphragms, and acts in a manner similar to an air-lift to induce through this channel a flow of electrolyte in the direction indicated by the arrows. The rate of this flow, the purpose of which is to wash the diaphragm and to prevent any fall of concentration around the anode, depends upon the current density, and under proper conditions attains several feet per second. Uniform concentration is maintained.

As stated, the inactive face of the pervious cathode is immersed in a liquid which is immiscible with the caustic solution and chemically inert toward it. The hydrogen which is liberated at the cathode escapes into the oil and thence upwardly through the narrow channel afforded by the plate 7, and sets the body of oil in extremely rapid circulation. At high current densities, in excess of 100 ampères per square foot of electrode surface, the rapidity of this circulation is quite striking.

The oil acts as a seal to prevent carbonating the caustic, as a support for the diaphragm (which may be of extreme thinness), and by its partially balancing hydrostatic pressure it tends to equalize the flow of electrolyte from top to bottom of the diaphragm; but its chief function relates to the quick removal of the caustic from the electrolytic field. Caustic solution does not adhere to surfaces wetted with oil, and therefore the caustic does not accumulate in the cathode nor flow down the cathode in proximity to the chlorinated liquor. Instead it is projected by the escaping hydrogen into the oil in the form of minute globules and deposited under the oil at the outlet of the cell.

If this removal of the caustic were instantaneous neither hypochlorite nor chlorate, derived from this source, would be found

in the anode liquor. The data following represent the composition of the anode liquor in a cell having about nine square feet of active anode surface. The experimental run was continuous from August 14th to September 7th, the anode liquor being sampled daily.

Date	Amp.	Cl Grams per Liter	ClO Grams per Liter	ClO^3 Grams per Liter	
Aug. 14	1000	. .	. . .	. . .	Start 3.30 P.M.
" 15	"	0.57	0.084	0.424	
" 16	"	0.14	0.154	0.0	Analyzed Aug. 18
" 17	"	0.26	0.0	0.0	" " "
" 18	"	0.35	0.105	0.0	
" 19	"	0.64	0.07	0.0	
" 20	"	0.355	0.091	0.0	
" 21	"	0.41	0.091	0.0	Analyzed Aug. 23
" 22	"	0.28	0.028	0.0	" " "
" 23	"	0.50	0.133	0.0	
" 24	"	0.53	0.091	0.0	
" 25	"	0.55	0.091	0.0	
" 26 A.M.	1200	1.02	0.154	0.368	
" 26 P.M.	"	1.03	0.21	0.440	
" 27	"	0.50	0.077	0.088	
" 28	"	0.43	0.0	0.0	
" 29	"	0.46	0.133	0.0	
" 30	"	0.57	0.063	0.0	
" 31	"	0.57	0.119	0.0	
Sept. 1	"	0.51	0.119	0.0	
" 2	"	1.065	0.049	0.088	Analyzed Sept. 12
" 3	"	0.19	0.119	0.224	" " 15
" 4	"	0.46	0.0	0.072	" " "
" 5	"	0.28	0.0	0.104	" " "
" 6	"	0.28	0.028	0.128	" " "
" 7	"	0.38	0.07	0.144	" " 12

The samples of September 2d-7th, inclusive, were analyzed after standing for several days in bottles exposed to the light. The traces of chlorate shown in these particular analyses were in all probability produced during this period.

During the run the cement walls of the anode compartment were attacked to a considerable extent, some calcium and magnesium appearing in solution, and hydrated silica in suspension in the anode liquor. It is by no means certain that the persistent traces of hypochlorite shown by the analyses, never rising to 2/100 per cent., and seldom entirely disappearing, existed as the sodium salt. It is quite possible that the hypochlorite is attributable chiefly to the action of the chlorin on the cement, more par-

ticularly because it reaches its maxima at the very beginning of the run, and whenever the wash of the anode liquor is increased by raising the current density.

The above results should correspond to substantially pure chlorin. The samples collected showed 99.7 to 99.8 per cent. Cl, subject to a correction of unknown magnitude for the aeration of the anode liquor which, under the particular circumstances, was unavoidable. The effect of this and other errors affecting the analysis would be to increase the above chlorin value.

Caustic efficiency: The anode liquor carried about 0.55 grams per liter of dissolved chlorin. This is the solution which oxidizes the cathodic deposit of sodium, for, as will be apparent, the cell has no distinct cathode electrolyte. The dissolved chlorin in a volume of solution corresponding to the actual outflow through the cathode would correspond to a loss of caustic amounting to about 0.4 per cent. of the theoretical yield for 1,000 ampères. We should therefore expect a caustic efficiency not to exceed 99.6 per cent. of theory. All caustic solution produced throughout the run was weighed and analyzed, but the errors incident to sampling and current measurement were sufficient to mask this presumably necessary loss, the apparent caustic efficiency being in slight excess of the expected result.

In the *Electrochemical Industry* for December, 1902, the writer gave some data as to the sodium chlorid content of certain electrolytic caustic soda lyes. At that time it was not considered advisable to describe the cell other than by the statement then made that "it was provided with a thin permeable diaphragm, adapted to restrain and equalize the flow of the electrolyte, and a cathode whose form fitted it to serve as a surface for the rapid discharge of the cathode products." This possibly somewhat inadequate description of the present cell gave rise to a misconception which led to a criticism* of the article on the ground that two essential conditions had been overlooked, to wit: the concentration changes which take place around the electrodes when sodium chlorid solution is electrolyzed in the anode and cathode compartments of a diaphragm cell, and the migration velocities of the hydroxyl ions when the formed caustic participates in the electrolysis. It will now be clear that the reasons for not con-

* Trans. American Electrochemical Society, Vol. 3, page 177.

sidering these factors were, first, that the caustic is formed by oxidation of sodium in a homogeneous chlorid solution maintained at constant concentration, and second, that the "rapid discharge of the cathode products" is sufficient to guard against the entry of the caustic into the electrolytic field.

DISCUSSION.

PRESIDENT CARHART: Are there any remarks to be made?

DR. J. W. RICHARDS: I would like to ask Mr. Townsend what it is which prevents the sodium chloride from passing into the caustic soda which is formed, and what is the commercial means of separating the caustic soda and obtaining it free from chloride?

MR. C. P. TOWNSEND: No means are provided for preventing sodium chloride from passing into the caustic, which as it comes from the cell is nearly but not quite saturated with salt. This salt separates quite readily on evaporation, 1 per cent. or less remaining in the hot solution at 50° Be.

A paper read at the Seventh General Meeting of the American Electrochemical Society, held at Boston, Mass., April 25, 1905. President Carhart in the chair.

CONDUCTION IN FUSED AND SOLID ELECTROLYTES.

By Joseph W. Richards.

The extent of the subject which it was at first intended to discuss, viz., conduction in electrolytes, became too evident, and the present paper will discuss only some phases of conduction in melted and solid electrolytes.

The term molten electrolytes is logically a misnomer, if it is intended by it to mean those electrolytes to which heat must be applied to melt them, and which become solid at ordinary temperatures. Temperatures are essentially relative, and if the prevailing temperature were some 250° or 300° Centigrade, many easily melting salts would be conductors and easy to electrolyse at what would then be ordinary temperature. I believe that there is no essential difference in the manner of the electrical conductivity of a salt which fuses at 200° C., or even at 0° C., and another which happens to melt at a red heat. If anyone thinks that there may be some essential difference, I should be glad to have it mentioned in the discussion.

When we melt a salt it conducts electricity comparatively well. As it cools it conducts more poorly, as it sets its decrease of conductivity continues, and after setting it generally conducts a measurable quantity of electricity down to some 300° or even 600° below its setting point, when its conductivity becomes generally very small. This is the general behavior of an oxygen or halogen salt. There is practically no break at the setting point; there is no change *"per saltum,"* as the material passes from the liquid to the solid state, or *vice versa.* The evidence is unquestionably that, whatever the nature of the property of electrical conductivity in the fluid state of such salts, the conductivity in the solid state is essentially of the same kind or nature.

I have drawn in Fig. 1 the curves of electrical conductivity of several salts, from data given in Ostwald's Allgemeine Chemie,

volume on Chemische Energie. The circles on the curves mark the melting points of the salts. The conductivities of most of these salts become practically zero within 250° of the melting points. I have detected measurable conductivity in solid sodium

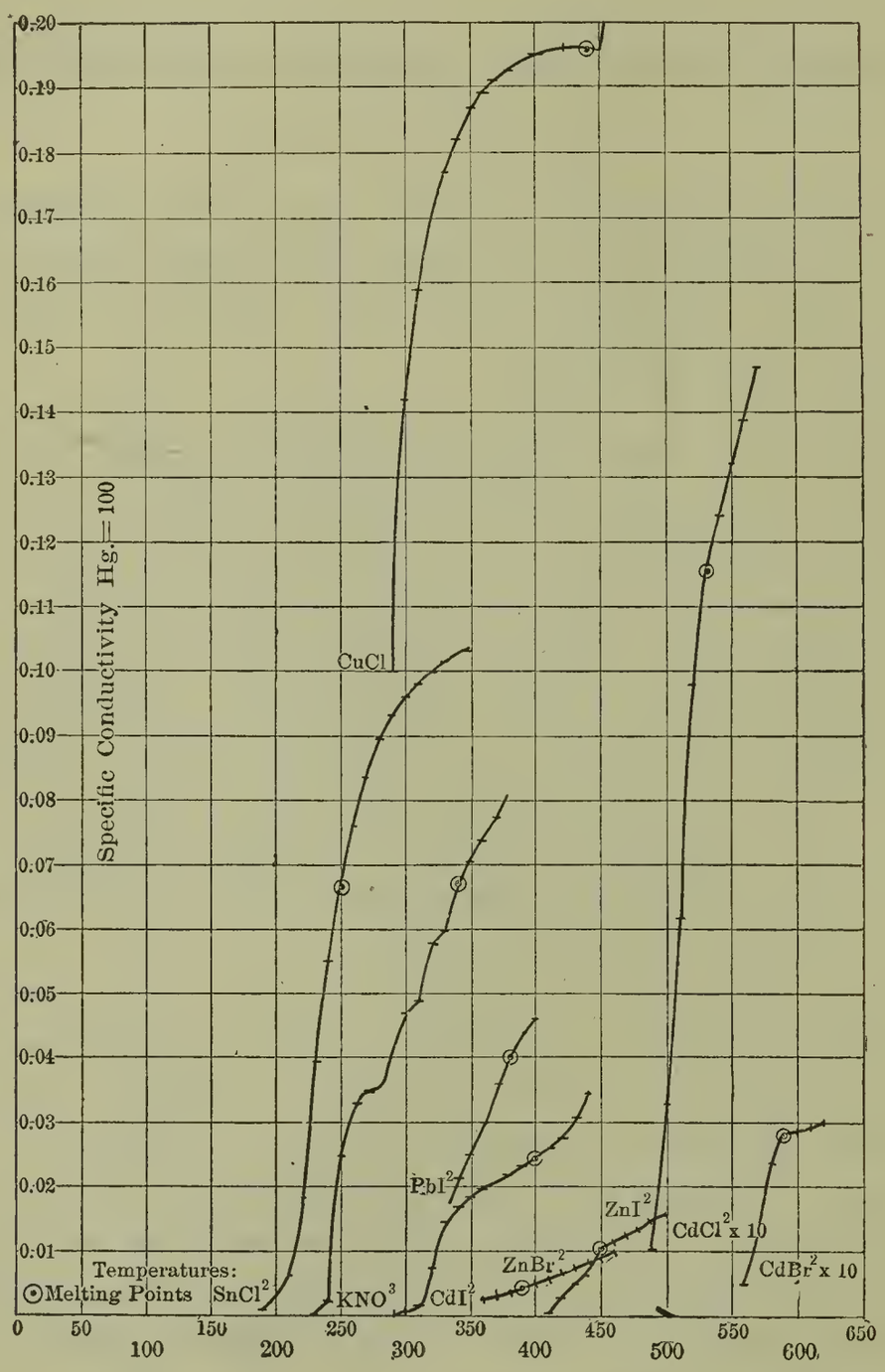


FIG. I.

carbonate at 600° below its melting point, while Haber and Tollozco have passed currents continuously through solid barium chloride 500° below its melting point.

There is therefore no possible doubt that the property of electrical conductivity of this class of salts is a property which begins

to be measurable at several hundreds of degrees below the melting point, and passes without essential change straight through the melting point, so that we can safely postulate that *"the conductivity in the melted condition is essentially of the same nature as in the solid condition."*

Everything points therefore to the fact that in these salts their electrical conductivity is a property which is essentially dependent for its existence upon some sort of freedom of molecular motion or diffusion, which increases with increasing temperature. Or, in the language of the phase rule, the electrical conductivity seems to come into existence when the possibility of new phases is caused by the increase of temperature.

What are the facts regarding the electrolysis of these fused salts? They appear to show, first, that most of these salts have a very strong power for dissolving the metal which is their base. Lorenz has called these solutions *"metallische schliere,"* "metallic veils," since they float down from the cathode like a mist. Such phenomena are probably just what they appear to be, viz.: solutions (like colloidal solutions) of the metal itself in the liquid salt. In other cases, a metallic veil does not form, but the metal at the cathode very rapidly goes into solution, evidently as a lower salt, such as Na^2 Cl in Na Cl, which is capable of mixing in or mutually dissolving in the original salt in all proportions. Again, at the anode, there is undoubted evidence of the ability of the fused salt to absorb or dissolve the anion, and either to simply hold it in solution (like chlorine dissolved in salt solution) or to form more acid compounds which mix with or mutually dissolve in the original salt in all proportions.

This ability of the salt to form other phases is a powerful one, as may be judged from the fact that caustic soda must be electrolysed within 30° of its melting point in order to get sodium, and that above that a 1,000-ampère current in an eight-inch pot causes no metal to separate out. The tendency is so powerful that, if properly understood, it may be found quite active enough to account for all the phenomena of the so-called "migration of the ions," although very few have been bold enough to attempt to explain conduction in fused salts by the usual ionic mechanism.

In electrolysing fused caustic soda, not only does metallic

sodium dissolve in the melt, but the solution formed diffuses away from the cathode with extraordinary rapidity, so that not a trace of sodium is left undissolved, although 1,000 ampères are sending it out on a four-inch cathode. It may be that the oxygen at the other pole also dissolves with great rapidity, forming a higher oxidized phase radiating from that pole. In any case, either the first or the second, or both assumptions, would account for the phenomena. Or, another point of view might be taken: At the cathode the current extracts sodium, leaving the salt in the acid phase, that is, with the chemical equilibrium of the phase-caustic soda disturbed in the direction of less base, or, relatively, more acid. This relatively acid phase diffuses in the melt, and thus carries oxygen towards the other pole. At the anode the extraction and evolution of oxygen leaves the melt with relatively less acid, *i. e.*, relatively more basic, or the equivalent of caustic soda plus dissolved sodium and hydrogen, and this diffuses towards the other pole, thus carrying the sodium towards the cathode.

According to these views, the electric current at the electrodes disturbs the chemical equilibrium and introduces, or at least accentuates, a new phase in the melt; it extracts acid at the anode and leaves the melt there with a basic phase; it extracts base at the cathode, and leaves the melt there with an acid phase. These two new phases diffuse with great rapidity in the melt, and thus carry the acid ingredient towards the anode and the basic ingredient towards the cathode. They are also capable of reacting upon the substances separated upon the electrodes, the velocity of this reaction increasing rapidly with the temperature, and when they re-combine with them as fast as they are separated upon the electrodes, the current passes without apparent electrolysis.

When such a salt sets, electrolysis does not immediately cease. Faraday, with silver sulphide; Kohlrausch, with silver chloride; Haber and Tolozco, recently with barium chloride, and numerous investigators with Nernst lamp glowers, have proven that not only electric conduction, but also electrolysis, takes place in the solid materials at hundreds of degrees below their melting points. In these cases the explanation of the electrolysis is the same as above given; two new phases are developed at the electrodes, and these phases diffuse through the solid material, in what is now a well-

known manner. The power of lead to diffuse through gold, hydrogen through platinum, or, more to the point, of carbon to diffuse into solid iron, or to diffuse out again, if the temperature be high enough, or numerous other illustrations of diffusion of phases in already solidified material, are well known to the chemist. It appears to me that the principle is capable of furnishing the explanation of the phenomena of electrolysis of solid salts.

The question is not *malaprop:* "How about solutions?" Well, solutions are simply mixtures of two substances, the whole in the liquid state, and presenting at least two components to start with. The solution melts usually at a lower temperature than its ingredients, is completely liquid, and is usually a conductor. When there is a possibility of the reducing action at the cathode and the perducing action at the anode producing a shifting or creation of new phases, which are themselves soluble and diffusible in the original liquid, than electrolysis is possible, and the "migration of the ions" is kept up by the diffusion of these acid and basic phases from the cathode towards the anode, and *vice versa.*

At the present time there is considerable uncertainty regarding the proper theory of electrolysis. The dissociation theory applied to solutions at ordinary temperatures has appeared to the majority of electrochemists as a satisfactory theory; but to many others it has never been satisfactory, its weakest point being fused salts, which are good electrolytes, and yet not solutions. And no one, not even the originators of the theory in question, would apply it to solid salts, and yet the latter are electrolytes. (Ostwald says: " . . . festen Salzen, die nicht electrolytisch dissociert sind.") May not the present view, of displacement of phases, or creation of new phases, at the electrodes, coupled with the known diffusibility of phases in liquids, and even in solids, account for the phenomena of electrolysis and the so-called "migration of the ions?"

DISCUSSION.

President Carhart: This interesting subject is open for discussion. We would be glad to have any gentleman interested in the subject contribute.

I wanted myself to ask a question—perhaps I did not listen attentively enough to catch all Dr. Richards said, my mind being necessarily otherwise engaged. As I understand, he explained what follows upon the passage of a current. What I do not understand is, how the current passes in the first place, before these changes take place which are produced by the current.

PROF. FRANKLIN: Your comment is exactly what I had in mind to say—that it seems to me that the rôle played by diffusion is subsequent to the primary electrolytic processes; at least I have always thought of diffusion actions as being the explanation of the absence of genuine electrolytic effects in the Nernst filament, for example. We say that this is electrolytic conduction: but there is no metal which continues to appear at the cathode and no anion appears to be liberated at the anode. We have brought diffusion effects into account as an explanation of the absence of those results that are generally associated with electrolysis.

DR. W. R. WHITNEY: It seems to me that we are in danger of confusing the phenomena of electrolysis (*i. e.*, the phenomena taking place at the electrodes) with conduction through the electrolyte. This danger has been pointed out a great many times. In this case, if the electrolyte were made long, as it could be by being enclosed in a long tube, and if what goes on in the middle of the tube could be studied independently of the effect of simple diffusion from the electrode, much light could be thrown on the subject. If the fusions at the electrodes were connected together in a long tube having in its middle portion a solution of copper sulphate, you will find that the copper and sulphate ions will migrate immediately on closing the circuit, and this independently of any phenomena taking place at the electrodes, *i. e.*, independently of the products of the electrolysis.

PROF. T. W. RICHARDS: It seems to me that in one case in particular, namely, the case of the electrolysis of silver nitrate between two silver electrodes, where the silver is dissolved out quantitatively on one side and precipitated quantitatively on the other side, and the electrolyte stays perfectly constant in composition throughout, this interpretation is inapplicable.

PRESIDENT CARHART: Did you find the anodic loss in this case the same as the gain of the cathode?

PROF. RICHARDS: It is the same as nearly as it was

determined. We made no very precise measurements—much less powder separates from the anode than in the case of aqueous solution, and the conditions are therefore more favorable to accuracy in the case of fused salts.

Dr. J. W. Richards: I think I studiously avoided saying in the paper anything which would imply that I knew just how electricity passed through the cell; I wish I did. The more I study electrolytes the more convinced I am that the manner of the passage of the electricity through the body of the electrolyte itself is identical in metals, fused salts, and solid salts, and whatever the method of conduction of electricity through matter is, I am impressed with the thought that we have not any certain proof or satisfactory proof that it is different in these different materials. Present theories have not appeared satisfactory to me, and the facts as I have studied them seem to show that the material acts simply as a conductor; and my explanation was directed towards the question, How do the two separate products separate out at the two poles; what is the phenomena of electrolysis in these melted and solid salts? I will say for myself that the study of the theory of electrolytic dissociation gives a very satisfactory picture of how things may happen in a solution. If we grant the premises there seems to be for solutions very satisfactory—mentally satisfactory—explanations of the phenomena, but when it comes to a melted salt which is 100 per cent. itself—where there is no question of the solution of one thing in another—or when it comes to a solid salt, it seems to me that the phenomena in the electrolyte (that is, the separation out of the two ingredients at the two poles and the transfer of the constituents of the material, bodily, from one electrode to the other) is capable of being explained by these phenomena of the diffusion of different phases through the solid or the liquid material.

A paper read at the Seventh General Meeting of the American Electrochemical Society, held at Boston, Mass., April 25, 1905. President Carhart in the chair.

NOTES ON NERNST FILAMENTS.

BY C. I. ZIMMERMAN.

The Nernst filament is frequently thought of as a typical example of a solid electrolytic conductor. It is the purpose of these notes to show that we do not have here a case of plain electrolytic conduction.

Direct evidence of electrolysis is present, although in the commercial type of the Nernst glower the decomposition is purposely reduced to a minimum. Electrolysis is more marked at current densities considerably below the normal than at or above the normal. At low current densities there may be observed at the cathode a core of dark metallic material which has a high conductivity. As a result of the increased decomposition at low current densities, a direct current glower has a short life at very low temperatures.

At the anode there is a liberation of heat. At the cathode there is an absorption of heat. These effects are similar to the Peltier effects observed at the junction between two different kinds of metals. So great are these thermal effects that an anode of platinum (melting point 1,760° C.) may be melted, while a cathode of silver (melting point 960° C.) remains solid.

The cathode metal is absorbed by or possibly projected into the glower material toward the anode. The presence of silver, platinum or other metals has been detected by chemical analysis at considerable distances from cathodes consisting of those metals. This effect is distinct from the metallic core noted previously.

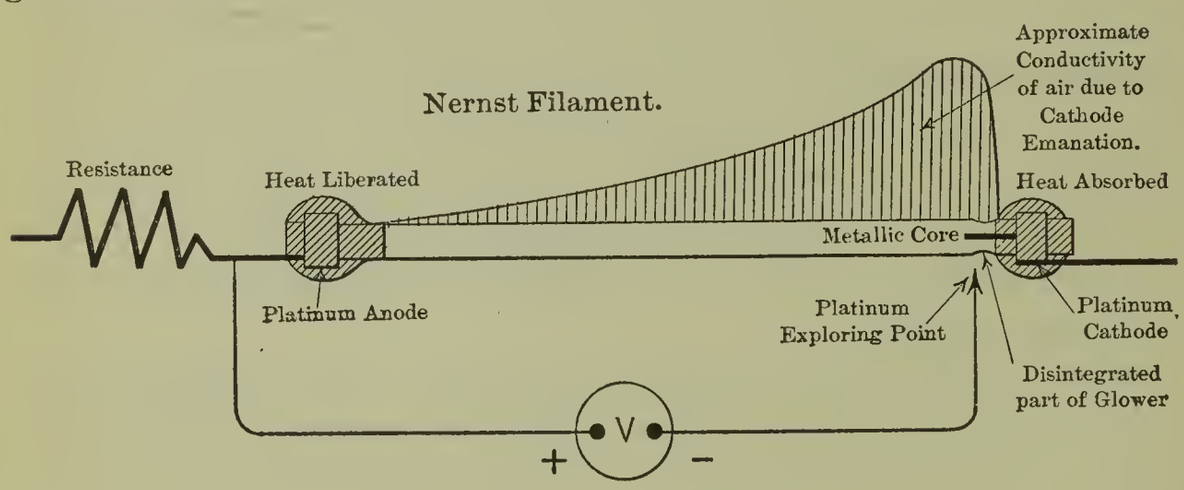
Close to the cathode of a D.C. glower a constricted portion is observed after the glower has been operating for some time. This is apparently due to a disintegration of the oxides by some cause other than electrolysis. Reversing the polarity of a Nernst glower shortens its life materially.

The conductivity of the air in the neighborhood of a Nernst glower has been alluded to at various times. It can be readily

shown to be due almost entirely to a "negative electrode phenomenon."

The following few simple experiments plainly illustrate this effect:

A 200-volt Nernst glower (either A.C. or D.C. type) and a Weston (0 — 300 volts) D.C. voltmeter are connected together at their positive terminals. The free lead of the voltmeter is used as an "exploring wire" to note the leakage through the air. When a direct current passes, deflections as high as 50 volts may be observed when the wire is held close to the glower and about 3-32 inch from the negative electrode. The approximate distribution of the conductivity of the air due to the negative electrode effect is shown in the sketch by the shaded lines perpendicular to the glower axis.



In general, the effect is more marked as the temperature is increased. With the negative terminals of the glower and the voltmeter connected together no deflections of the needle are observable, although the temperature of the air near the point of the exploring wire is greater than it was in the previous case. Evidently it is not the extreme temperature of the air that makes it conducting.

The same effects are observed in a more convincing way with the glower operating on A.C. The needle of a D.C. voltmeter will show a marked deflection with the connections the same as in the previous cases. The polarity of the current is observed to be such that the leakage through the air occurs when the permanent connection between the voltmeter and the glower is the momentary positive end.

Electrostatic instruments show "leakage" from both electrodes, but that from the negative electrode is the greater in magnitude. The predominance of the negative electrode leakage is strikingly manifested with a Kelvin multicellular electrostatic voltmeter connected as the other meters previously were.

A 200-volt A.C. Nernst glower (commercial type) can produce a deflection as high as 250 volts.

This deflection can be readily shown to be due to a unidirectional static charge. The static charge is received during the half-cycle when the exploring wire is near the momentary negative electrode of the glower. A charge once received from the "peak" of an alternating wave cannot leak off rapidly, and the voltmeter, therefore, indicates a deflection higher than the effective value of the A.C. voltage on the glower terminals. These particular conditions for high voltage deflections are similar to those present in unsymmetrical aluminum electrolytic condensers.*

Pittsburg, Pa., April, 1905.

* See "The Aluminum Electrolytic Condenser," these Transactions.

A paper read at the Seventh General Meeting of the American Electrochemical Society, held at Boston, Mass., April 25, 1905. President Carhart in the chair.

ON BILLITZER'S METHOD FOR DETERMINING ABSOLUTE POTENTIAL DIFFERENCES.

By H. M. Goodwin and Robert B. Sosman.

In an interesting article on "Absolute Potential Measurements," which appeared in Drude's Annalen,[1] in 1903, Mr. J. Billitzer describes three new experimental methods of determining the absolute potential between a metal and a liquid, and presents results obtained by these methods which, although sufficiently concordant among themselves, are completely at variance with those generally accepted, based upon the well-known surface tension phenomena. The magnitude of the discrepancy may be judged of by the fact that the value of the potential of a normal calomel electrode determined by the proposed methods is 0.74 volt above the value generally assumed. To explain this discrepancy the author suggests a modification of Helmholtz's double layer theory, namely, that the opposed charges of a double layer are not, as heretofore assumed, equal, but that a positive or negative charge according to circumstances preponderates.

The theoretical importance of the questions thus raised by the results of this investigation seemed to us to make a further verification of the experiments on which the conclusions of the article are based, desirable. With this in view we undertook to repeat with as great care as possible the experiments described. As the exact conditions under which the experiments were carried out, particularly as regards the concentration of the solutions used, are stated very vaguely by the author, it was difficult or impossible to know what the exact conditions were. We have attempted, however, to reproduce them as nearly as possible. It may be stated in advance that our experiments do not furnish a satisfactory confirmation of the results in question.

[1] Ann. der Phys., *11*, 902, 927 (1903).

THE PROPOSED METHODS.

The line of reasoning on which the proposed methods are based may be briefly stated as follows: If a minute metallic ball or particle be suspended in a liquid between which and the particle a difference of potential exists, there is formed at the surface of contact of the two a double layer (Helmholtz.) The metal may possess a positive or negative charge with respect to the liquid depending upon the electrolytic solution pressure of the metal (Nernst), and on the concentration of the ions of the metal in the solution. If such a suspended ball or particle, supposed positively charged, be placed in the path of a strong potential gradient maintained from an external source by immersing two electrodes in the liquid, the positive charge on the particle will be attracted to the negative electrode or cathode, and the negative charge of the double layer in the liquid will tend to move in the opposite direction to the positive pole or anode. A motion of the particle in the direction of the current, *i.e.,* towards the cathode, should result. If the polarity of the double layer be reversed, the motion should be in the opposite direction. If the potential between particle and liquid is zero, *i.e.,* the double layer disappears, there should be no motion. Electrostatic effects arising from induction due to unsymmetrical disposition of the ball with respect to the electrodes are of course supposed to be eliminated by observing with reversals of the polarity of the electrodes producing the field. Absence of motion of a particle or minute metallic ball suspended in a liquid through which a potential drop is maintained is taken therefore as indicating zero potential between the metal in question and the liquid, and if an auxiliary electrode of the same metal as the suspended particle be immersed in the liquid the potential between it and the liquid is also assumed zero. Such an electrode can then be used as a standard of reference in combination with other electrodes to determine the absolute potential difference between them and the solution in which they are immersed respectively.

The three following methods, all based on this principle, are proposed. The essential difference between them is the mode of observing the reversal point or disappearance of the double layer.

I.—The deflection of a minute ball fused at the end of fine wire and suspended in a liquid by a quartz fibre is noted.

II.—The direction of migration of a colloidal metallic suspension is noted.

III.—The potential difference produced at the ends of a tube of liquid when a metallic suspension is allowed to fall through the liquid is noted.

In the experiments described by Billitzer all three methods lead to practically the same result, namely, that a reversal of motion in case I and II, and a reversal of potential in case III occurs when the potential between the auxiliary electrode in the solution under investigation and a 0.1-normal calomel standard electrode is +0.125 volt, or, in other words, assuming the P. D. at the auxiliary electrode to be zero, the P. D. (solution to metal) of a 0.1 calomel electrode is +0.125 volt, *i. e.*, 0.74 volt greater than 0.614 volt, the value usually assumed.[2]

In the present paper we have repeated the experiments made by the first method. The experiments described under the second method have at the same time been made the subject of an investigation by Dr. J. C. Blake, in connection with an extended research on colloids.[3] The results obtained by him failed completely to confirm those obtained by Billitzer, for it was found that the direction of migration of the metallic colloid (Bredig) could be varied at will by the addition of a greater or less amount of gelatine which it was necessary to add to prevent coagulation of the colloid when an electrolyte was added to the solution. Billitzer also used gelatine for this purpose in all of his experiments, but he fails to state in his article exactly how much was added. In his paper *"ein spur"* is stated as being sufficient, while in a letter to Blake he states that *"recht viel"* was added.[3] The reversals observed by Billitzer in these experiments would seem, therefore, to be due to the variable gelatine concentration rather than to the disappearance of the double layer on the suspended particles, and hence his conclusions relative to the potential of reversal, so far as they rest on experiments based on the second method, do not appear to be warranted.

[2] Billitzer erroneously adopts in his computation the P.D. of a normal calomel electrode instead of that of the 0.1—normal electrode, which he used in his experiments, *i.e.*, he bases his potentials on the value —.277 volt (normal hydrogen electrode = 0) instead of the correct value —.337 volt. The value used is moreover incorrect; it should be taken as —.283 volt. (Wilsmore, Zeit. für Phys. Chem., *36*, 91 (1901).

[3] Am. Jour. Chem. Soc., Sec. *26*, 1378.

In view of the above results and those described below, the third method has not been further investigated.

A description of the apparatus used, procedure, etc., may be found in a detailed discussion of the experiments, which will appear shortly in the *Physical Review*. A summary of the chief results obtained are here presented.

As regards the procedure, it need only be stated that the attempt was made to repeat the conditions of the experiments described by Billitzer as exactly as possible from the description given. A potential gradiant of 110 and 220 volts was used for producing the deflections; great precautions were employed in securing steadiness of the suspended system; both platinised and polished platinum electrodes were used as auiliary electrodes in the solutions investigated, and their potential was measured against a standard 0.1-normal calomel electrode by the Poggendorff computation method, using a Lippman electrometer sensitive to 0.001 volt as indicating instrument. In expressing the following results a motion of the suspended wire towards the anode is recorded as *negative;* when towards the cathode, *i. e.,* in the direction of the current, as *positive.*

EXPERIMENTAL RESULTS.

I. Qualitative experiments on the direction of the deflection produced with platinum wire (0.025 mm. diameter) suspended in various liquids, gave the following results: In air, distilled water, and water plus a trace of salt, acid, or bromine, the deflections were negative, indicating the platinum to be negatively charged with respect to the liquid. These results agree with Billitzer's observations. In formaldehyde, ether and chloroform the deflection was positive, as found by Billitzer. In the case of ethyl alcohol and hydrogen peroxide we found the platinum to be negatively charged, while Billitzer, on the other hand, found it to be positively charged. With acetone the exact converse was the case—we observed a positive, and Billitzer a negative deflection. The qualitative agreement between our observations and his can therefore be said to be only approximate.

II. Passing to quantitative experiments in which the concentration of the liquid was varied over wide limits by the addition of

oxydizing or reducing agents, in order to establish the condition of the disappearance of the double layer, we first tried aqueous alcohol solutions. With concentrations varying from 96 per cent. to 32 per cent. alcohol the deflections observed were all negative, *i.e.,* indicating the platinum wire to be negatively charged vs. the solution, while Billitzer obtained for this range of concentrations positive deflections. He observed, however, a reversal in the deflection when the auxiliary platinum electrode registered against a 0.1 normal electrode +0.15 volt to +0.139 volt. Such a reversal we were unable to obtain, although our platinum auxiliary electrodes showed approximately the same values vs. 0.1-normal calomel electrode. As pure water itself gave in all of our experiments negative deflections, no reversal could be obtained in passing from 96 per cent. alcohol to pure water.

III. Solutions of hydrogen peroxide gave similar results. Billitzer observed a reversal of deflection when his auxiliary electrode registered 0.12 volt. Unfortunately, at what concentration this occurred is not stated, in fact even approximate concentrations are not indicated. We obtained negative deflections in all cases with solutions varying in concentrations from 0.001 per cent. to 2 per cent.

IV. In the case of formaldehyde Billitzer again observed a reversal when the potential of platinum vs. 0.1-n. calomel electrode was + 0.13 volt, no data being given, however, as to the corresponding concentration of the solution. We, therefore investigated a series of solutions varying in concentration from 40 per cent. to 0.04 per cent. In the most concentrated solutions up to 36 per cent. the deflections were positive. They became reversed in a 10 per cent. solution, and remained negative from that dilution on. The potential of the auxiliary electrodes did not, however, check Billitzer's + 0.13 volt value, being about — 0.04 volt for the platinised electrode and + .06 volt for the polished electrode.

V. Solutions of mixtures of ferrous and ferric salts were next investigated. Billitzer's +0.125 volt reversal potential could not be duplicated; the deflections observed were in all cases negative, although the relative concentrations of the ferrous and ferric salts were varied through wide limits.

VI. A mercury electrode in a solution of mercuric nitrate was next tried in place of the platinum. The suspended electrode was

prepared by depositing mercury electrolytically on the platinum ball previously employed. The deflection of the suspended ball changed from plus to minus at a concentration between 0.13 per cent. and 0.025 per cent. The auxiliary mercury electrode vs. 0.1-normal calomel electrode gave a corresponding potential of about + 0.57 volt. Billitzer obtained a reversal in a single case only with mercury, namely between 0.2 and + 0.08 volt for mercury — vs. 0.1-normal calomel electrode.

VII. Replacing finally the suspension by a very fine silver wire (0.043 mm. diameter) and using a silver auxiliary electrode in a solution of silver nitrate from which the silver ions were gradually removed by the addition of potassium cyanide, all deflections were found negative even though the concentration was varied until the potential of the auxiliary electrode vs. 0.1 normal calomel electrode reversed its potential from +.35 volt to —.30 volt. Billitzer failed to get a reversal by diluting silver nitrate with water, but in a series of experiments by his migrating colloid method, in which cyanide was added, he obtained a reversal between +.11 and +0.10 volt.

DISCUSSION.

A consideration of the preceding results indicates that—

First—The phenomenon in question, *i. e.,* of the reversal in deflection of the suspended wire, does not appear to be general, but occurs only in exceptional cases. The general phenomenon would seem to be a motion of the suspended metal towards the *anode.*

Second—The reversal phenomenon does not appear to stand in any definite relation to the potential between the auxiliary electrode and the solution, the characteristic reversal potential of + 0.125 volt vs. 0.1-normal calomel electrode found by Billitzer being in no case observed.

These two experimental facts seem to us to be reasonably well established by our experiments. We do not attempt to offer an explanation for the remarkably concordant results of Billitzer leading to entirely contrary conclusions. It is possible that some essential condition was observed in his work not sufficiently stated in his article to enable us to duplicate it in our experiments. If so we trust that it will be more clearly pointed out. Attention

may be called, however, to several factors which impressed themselves upon us in the course of our work, which have a direct bearing on the problem under discussion and which may lie at the foundation of the results observed.

EFFECT OF ELECTRODE SURFACE.

Does the auxiliary electrode indicate the same potential as that existing between the fine suspended wire and the same liquid? This is evidently a fundamental question, as the interpretation of all results obtained by Billitzer rests on the assumption that the two are identical.

We carried out several experiments to test this point by comparing against a 0.1-normal calomel electrode the potential drop between a platinized electrode, a polished electrode and an electrode consisting of a fine wire used for the suspension. It might be expected that since the last is smooth wire with a fused ball at the end, it would comport itself electrometrically more nearly like the polished platinum electrode than the platinized electrode. It was found that potential measurements with extremely fine wire electrodes, and even with electrodes consisting of a bunch of such wires, were difficult to make and rather uncertain in their results. The following figures show that the potential of a fine wire electrode and a platinized electrode in the same liquid may differ by several hundredths of a volt, the former being always higher.

Solution	*Wire*	*Platinized*	*Polished*
Formaldehyde	+0.02	—0.0	+0.059
"	+0.10	+0.019	+0.041
Alcohol-water	+0.07	+0.050	
"	+0.12	+0.037	
"	+0.14	+0.086	+0.100

Polished electrodes were found to be far less certain in their behavior than platinized electrodes, as was expected, and it might be fairly assumed that the wire electrodes would show similar irregularities. Platinized electrodes, on the other hand, when properly prepared by treating as cathode in dilute sulphuric acid to reduce and remove residues of the platinizing liquid (Ostwald), then washed in boiling water, gently heated and finally allowed to stand in distilled water, always gave concordant results among themselves.

EFFECT OF TIME ON POTENTIAL EQUILIBRIUM.

A very marked effect of time on the potential of the auxiliary electrode was noted in some cases, which was different for platinized and unplatinized electrodes. This was most marked in the case of formaldehyde solutions, and was noticeable in all other solutions except hydrogen peroxide and mercuric nitrate.

A gradual change in the solution may account in part for the gradual rise in potential observed. The point to be noted however, is, that the time required to reach equilibrium was much greater in the case of the platinized than in the case of the unplatinized electrode, and if the unplatinized suspended wire comports itself like the polished potential electrode the same kind of uncertainty in its indications as to deflection would probably result.

The cause of the gradual rise of potential of the auxiliary electrode observed in distilled water was also investigated. The potential was lower in freshly boiled water than in water which had stood some time in the air; the effect was therefore ascribed at first to dissolved oxygen, but when pure air was passed through the boiled water to resaturate it, the potential fell instead of rising. This suggested at once that carbon dioxide caused the change. Carbon dioxide from the lungs was passed through the water, and the potential rose; this carbon dioxide was then washed out by a current of pure air, and the potential fell to the value first obtained in air-washed water. Then saturation of the water with pure carbon dioxide brought the potential up somewhat above that obtained in water which had stood in air. Tory and Barnes[4] have observed such an effect with platinum and ascribed it to the air; it may be possible to explain their results by the presence of carbon dioxide.

EFFECT OF LIQUID JUNCTION.

Of minor importance in the present investigation is the value of the potential difference arising at the junction of the 0.1-normal electrode and liquid under investigation. This is at best uncertain in experiments like the above, and although in many cases it is probably small, owing to the nearly equal migration velocities of potassium and chlorine ions, yet with the somewhat complicated

[4] Trans. Amer. Electrochem. Soc., 3, 95, (1903).

nature of the solution and solvents used and their extreme dilution it is possible that it may in some cases have attained a very appreciable value.

EFFECT OF DISSOLVED GASES ON THE SIGN OF THE DEFLECTION.

We would like to point out one other factor which seems to us of much greater importance on the phenomenon in question than the preceding, and one which apparently has not been considered by Billitzer. We refer to the phenomenon described and investigated in 1861 by Quincke,[5] who found that minute bubbles of hydrogen, oxygen and air act exactly like solid particles when suspended in a liquid and *migrated towards the anode* when a current was passed through an aqueous solution containing them. In turpentine, however, he found that all substances which he investigated (except sulphur) migrated *positively, i. e.,* towards the cathode. Now it was frequently observed in our experiments that no deflection was produced at the first instant the voltage was applied. After visible electrolysis had taken place and minute bubbles appeared in the liquid, a deflection of the wire became evident and the deflection was always toward the anode. This seems to us significant, for although it is true that deflections were repeatedly observed at the instant the current was established, and when no bubbles were visible on the end of the suspended wire, yet it is quite conceivable, and indeed probable, that in the process of immersing the wire in the liquid from the air, very minute particles of air might remain attached to it, or might separate out on it from the liquid. The following experiment, in the light of Quincke's results, seems to bear out the above hypothesis. The platinum wire was suspended in turpentine and deflections observed with 220 volts applied. They were unmistakably positive. The resistance of the cell was so high that the current was less than 0.00001 ampere. In distilled water saturated with pure hydrogen the deflection was distinctly negative. The presence of minute, even invisible, bubbles of gas on the suspended electrode, which may arise from gases in the solution, from the air or from electrolysis, seems therefore to offer a very plausible explanation of the results observed.

Another factor, which may also have at least a secondary influ-

[5] Pegg. Ann., *113*, 565 (1861).

ence on the deflections, is the possible motion of the liquid surface under the action of the applied voltage.[6] Such a motion of the surface was frequently noticed on closing the circuit, when the microscope happened to be focused so that the surface was in the field of view. Since a difference of potential exists between a liquid surface and the gas above it, such a motion does not seem apriori unlikely. This phenomenon is worthy of further investigation.

CONCLUSION.

The present investigation was undertaken in order to obtain a confirmation of Billitzer's results on absolute potentials by the method of deflections of a minute metallic electrode suspended in various solutions under the influence of an electric current. The results obtained have failed completely to confirm the measurements obtained by him, and we are forced to the conclusion that the method proposed is not to be relied upon for the purpose for which it was developed. This conclusion is further confirmed by the results obtained by Blake on the migration of colloids, who has also failed to confirm Billitzer's measurements using this method.

So far as our experiments go, it would seem that most of the phenomena observed may be explained on the assumption of the negative migration of gaseous particles in the liquid, as first demonstrated by Quincke in 1861.

We believe, therefore, that the result obtained by Billitzer by the above described method afford as yet no sufficient grounds for rejecting the generally adopted values for the potential of the normal (or tenth normal) electrode.

Since the above work was completed two other articles [7] have appeared by the same author, in which he has determined absolute potentials by investigating the phenomena of concentration changes produced by dropping electrode (first studied by Palmer), and by a modification of Pellet's surface tension method. As the results obtained by both of these methods confirm the author's previous results, in assigning approximately — 0.40 volt (normal hydrogen electrode =0) as the potential at which the double layer

[6] H. B. Kendrick, Zeitschr. f. Physikal. Chem., *19*, 625 (1895).

[7] Zeitsch. f. Phys. Chem., *46*, 513 and 542 (1904).

for mercury reverses its sign, or, in other words, in changing the usually accepted value of the normal calomel cell by — 0.7 volt, a description of the precise conditions under which the previous experiments were carried out seems all the more desirable.

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ON THE EDISON STORAGE BATTERY.

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INTRODUCTION.

The first article published on the Edison battery was a paper read before the American Institute of Electrical Engineers in 1901, by Professor Kennelly. In the time since elapsed the battery has been the subject of much discussion and experimental study, mostly from the technical standpoint. These articles are referred to at the end of this paper. The latest information as to the value of this battery as a storer of electrical energy is to be found in a recent article by Professor Kennelly and Mr. Whiting.[1]

The following points, interesting from a theoretical standpoint, include all that is known at present concerning the battery.

1. Charge and discharge curves.—These have been determined frequently.[2] On discharge the P.D. is at first constant at about 1.3 volts, then drops rapidly to 0.7 volt, where it is again constant, and then rapidly decreases to zero.

On charge, the P.D. generally shows a maximum point at the start. The cause of this is not known.

2. Potential change of plates on discharge.—It has been shown by Joly and by Jouaust that the nickel-plate changes, while the iron remains constant,[3] but what the single potentials of the plates are, is not given. In these measurements Joly used the case of the battery as the auxiliary electrode. Jouaust does not name the auxiliary electrode used by him.

3. Gasing.—For a type D cell, capacity about 165 ampère hours, Joly found a minimum in the rate of gas evolution after 100 to 125 ampère hours' charge, and again a maximum at 250. Kennelly[4]

[1] Trans. A.E.E.S., VI, 135.

[2] Hibbert, Jour. of the Inst. of Electrical Engineers, *33*, 203 (Jan., 1904).

[3] Joly, ibid.
Jouaust, Eclairage Electrique, *38*, 201.

[4] Loc. Cit.

states that in ordinary charging there is a maximum evolution of gas after quarter of an hour. Burgess[5] states that at the highest rate of discharge not enough gas is liberated to be measured.

4. *Effect of temperature on capacity.*—Hibbert[6] estimates that there is an increase of 0.26 per cent. per degree C, from runs not designed especially to measure this quantity.

Jouaust[7] has measured the change in capacity from 0°C to 50°C, and found it to be 30 per cent., that is 0.6 per cent. per degree.

5. *Change of resistance on discharge.*—No careful measurements have yet been made. Hibbert[8] finds that it remains constant during most of the discharge, but rises rapidly at the end.

6. *Current efficiency.*—This is given by Kennelly and Whiting as 75 per cent. for four-hour charge and discharge of an E 18 cell. Hibbert found 60 per cent. at 60 ampères and 56 per cent. at 100 ampères in the case of type D cell.

7. *Watt hour efficiency.*—This is given as 50 per cent. by Kennelly and Whiting.

8. *Self discharge.*—The following table is taken from the data in the article of Kennelly and Whiting.

Observer	Type of Cell	Percentage in loss	Time
At Edison Factory . .	——	15 per cent.	8 weeks
" " " . .	——	11 "	1 week
Hibbert	D	9 "	48 hours
"	"	27 "	26 days
Hospitalier	"	Less than 10 per cent	24 days
Kennelly & Whiting .	E 18	9 "	26 days

9. *Concentration changes at the electrodes.*—According to a theory worked out by Roeber,[9] considerable concentration changes must occur at the electrodes on charge and discharge of the battery. Schoop[10] has shown experimentally that these changes take place. It was found that during discharge the solution becomes

[5] Trans. A.E.E.S., VI, 150.
[6] Loc. Cit.
[7] Loc. Cit.
[8] Loc. Cit.
[9] El. World & Eng., *38*, 938.
[10] Elchem. Ind., *2*, 272, 310.

more concentrated in the pores of the nickel electrode, and more dilute in the iron. During charge the opposite effect is observed.

10. Temperature coefficient.—In a postscript to Schoop's article it is stated that Foerster found the temperature coefficient to be + 0.0007 volt per degree between 0° and 30°, and that this was independent of the concentration.

The following experiments were carried out in the Electrochemical Laboratory of the Massachusetts Institute of Technology. A portion of the work forms the graduation thesis of Mr. Richardson. The object was to throw some light on the reactions taking place in the battery, to measure the absolute potentials of the electrodes on the discharge, to measure the temperature coefficient and to study the effect of concentration of the electrolyte on the capacity and on the form of the charge and discharge curves.

EXPERIMENTAL PART.

The cells used in the following experiments were two of the type E 18. These were connected in series and readings taken on each as nearly simultaneously as possible. They were charged by means of lead storage batteries, through an adjustable iron wire rheostat immersed in water. The current and voltage were measured by means of calibrated Weston portable instruments.

The single potentials were measured by means of normal calomel electrodes and a Lippman electrometer, and are not connected for the potential of the liquid junction. There was a normal electrode for each cell. In the following tables the two columns headed "Bridge Pot" give the voltage measured of the normal electrode and one electrode of the battery. In case the electrode measured is cathode when combined with the normal electrode, this is indicated by placing the letter "c" after the measurement; if anode, the letter "a." This must be known in order to compute the single potentials.[1] In the plots the full curves refer to Cell No. 1; the broken to Cell No. 2.

The first of the following tables and curves gives the results on some charges obtained using the solution furnished by the company. These curves agree with those obtained by others. Following these charge curves are those obtained on discharge in the same solution plotted in Figs. 3 and 4. It is seen from these curves that during the whole discharge the iron electrode remains

[1] Lorenz, Elektrochemisches Praktikum, p. 167.

fairly constant at about + 0.5 volt. The nickel starts at about — 0.7 volt, is constant till the battery begins to fall to its second constant value. At this second constant part of the discharge the nickel electrode has a potential of from — 0.17 to — 0.20 volt, and as the battery potential falls to zero, the single potential of the nickel electrode approaches that of the iron electrode.

The steps for the nickel electrode then are

— 0.7 volt, — 0.18 to — 0.20 volt, + 0.35 to + 0.58 volt.

Measurements were now made to see if these potentials could be duplicated using known oxides of nickel.

From the fact that these potentials cannot be exactly duplicated in the battery itself, the difficulty of duplicating them with other materials is increased. In Table XI it is seen that NiO (obtained from Eimer and Amend) when mixed with graphite and placed in one of the nickel pockets taken from the battery, gives a potential in 25 per cent. KOH from — 0.15 to — 0.11 volt and Ni_2O_3 from — 0.37 to — 0.15. Comparing these with the value of the nickel electrode at the second constant part of the curve, it seems probable that either or both of these oxides are present and determine the potential. The final potential of the nickel plate is from + .35 to + 0.58. None of the oxides of nickel give a + potential. Nickel electrolytically deposited from nickel ammonium sulfate, however, had a potential of + .46 volt. This indicates that when the battery is completely discharged the nickel oxide is reduced to nickel.

The nickel electrode, then, when charged, is some high oxide of nickel not yet isolated. At the second constant part of the discharge curve this has been reduced to NiO, Ni_2O_3, or both. When fully discharged these oxides or hydrates are further reduced to nickel.

The fact that the iron electrode remains constant seems to show that even with twice the number of nickel plates its capacity is still greater than the nickel. Longer discharges of the iron plate, by replacing the discharged nickel plates by freshly charged ones, and continuing the discharge, would show whether the iron goes through different steps of oxidation. On drying a charged iron electrode and exposing to the air it becomes hot, showing that the plate in the charged state is finely divided iron.

One of the cells was now dismantled and smaller cells made up,

keeping the same ration of + to negative plates as in the original battery. A 50 per cent. solution of KOH (purified in alcohol) was made up and used in the new battery. The plates were given a short charge to make up for loss which might have occurred during handling and the discharge curve taken. The discharge was then observed. See Tables XI and XII and Fig. 5.

The batteries were then charged in a 50 per cent. solution. The solution was then diluted by one-half, and the discharge curves in the 25 per cent. solution taken. See Tables XIII and XIV and Fig. 6. They were then charged in the same solution, again diluted one-half and the discharge in the 12½ per cent. solution observed. See Tables XV and XVI and Fig. 7. The recovery for cell 2 was observed on opening the circuit. See Table XVII. For this dilution this is seen to be quite rapid.

The cells were then charged in the 12½ per cent. solution and discharged in a 6¼ per cent. solution. See Tables XVIII and XIX and Fig. 8. It is seen that for this strength of electrolyte the iron plate has lost nearly all of its capacity. The single potential of this plate changes, while the nickel plate remains constant.

It appears from this that the reactions which take place in dilute solutions on discharge are different from the reactions in the concentrated solutions.

The charge curve is also somewhat different. In the dilute solutions the maximum point at the beginning disappears. The amount of deposit issuing from the pockets was greater the greater the concentration. With a 50 per cent. solution the oozing took place even on open circuit.

It is seen from Table XX, when the voltages on open circuit for different strengths of the electrolyte are collected, that the voltage is independent of the concentration.

The measurements on the temperature coefficient are given in Table XXI. According to these observations the temperature coefficient is less the stronger the solution. That the temperature coefficient should change with the dilution does not agree with the theory that the electrolyte takes no part in the reaction. The accuracy in these measurements is not great, but it is greater than the difference in the values obtained for different concentrations.

These measurements do not agree with those of Professor Foerster communicated in the paper by Schoop, referred to above.

It was found by him that the temperature coefficient is independent of the concentration. This point therefore requires further study.

GAS ANALYSIS.

It seemed probable that more light might be thrown on the process of charging by analyzing the gases given off. This has already been proposed.[1] The following are some preliminary experiments in that direction. For this purpose four positive pockets and two negative were cut out of plates in the battery, and put in an Oettel voltameter in place of the usual electrodes. The wires holding the plates were nickel steel with a slit made at one end to hold the grid containing the pocket. The cell was then filled with a 20 per cent. solution of pure KOH to within a millimeter of the rubber stopper. The tube leading to the bath for collecting the gas was barometer tubing, so as to have the space unoccupied by the solution as small as possible. An Oettel voltameter was connected in series, and the gas from the battery and voltameter collected simultaneously.

It was observed that on starting the charging the nickel plate gased first. The normal current density was used, which required a current of 0.5 ampère for this battery. The gas was analyzed, and, assuming that the gas which escaped represented current loss, that the difference between this and the amount generated in the voltameter represented useful current, the curves shown in Fig. 9 were obtained.

When all the current is wasted in generating gas, the two efficiency curves should meet the axis. One electrolysis lasted six hours, and the battery even then did not give off as much gas as the voltameter.

The per cent. oxygen curve shows that as the charging proceeds the composition of the gas approaches that of detonating gas.

SUMMARY OF RESULTS.

1. The nickel plate when fully charged is some high oxide of nickel not yet isolated. This is reduced during discharge to Ni_2O_3 and NiO, both of which probably exist together at the second constant part of the discharge curve. When the battery is fully discharged the nickel oxide is reduced to nickel.

[1] Joly, loc. cit.

2. In 6 per cent. solution the iron electrode loses its capacity.

3. The temperature coefficient was measured and found to vary with the concentration of the KOH.

4. The open circuit potential of the fully charged battery is independent of the concentration.

5. The amount of material oozing from the plates increases with the concentration of the electrolyte.

6. It was found by gas analysis that the efficiency of charging the iron plate is greater than for the nickel plate in a 20 per cent. solution.

TABLE I.

Charge No. 1—Cell No. 1.

Time	P. D.	Amp.	Amp. Hrs.	Time	P. D.	Amp.	Amp. Hrs.
1.53	1.467	41.4	0	9.03	1.735	33.5	241
2.30	1.626	37.2	24.2	9.30	1.738	33.5	258
3	1.708	35.4	42.4	10	1.743	33.4	275
3.30	1.749	34.4	59.8	10.30	1.748	33.4	291
4	1.764	33.6	76.8	11	1.748	33.2	308
4.30	1.759	33.2	93.5	11.30	1.754	32.9	324
5	1.749	32.7	110	12	1.758	32.6	341
5.30	1.738	32.7	126	12.30	1.768	32.4	357
6	1.738	37.2	143	1	1.768	32.3	373
6.30	1.743	32.6	159	1.30	1.768	31.9	389
7	1.738	32.6	175	2	1.773	31.9	405
7.30	1.734	32.6	192	2.30	1.778	31.6	421
8	1.733	32.6	208	3	1.778	31.4	437
8.30	1.734	33.6	225	3.30	1.788	31.4	452

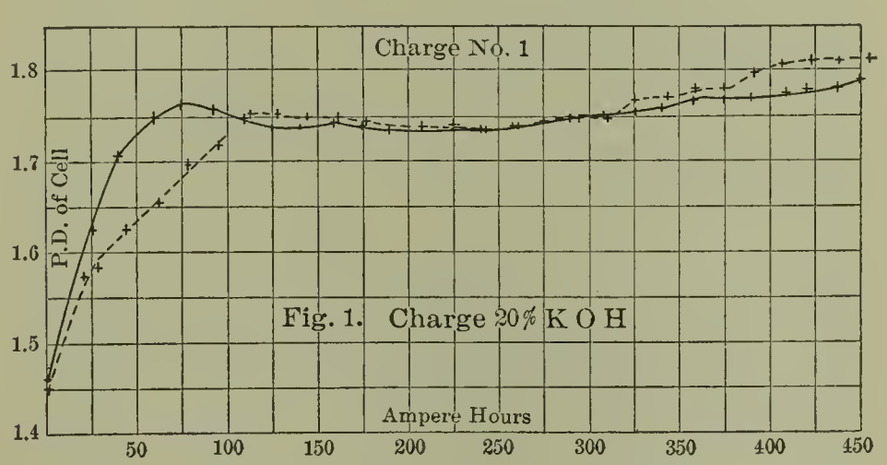


Fig. 1. Charge 20% K O H

TABLE II.

Charge No. 1—Cell No. 2.

Time	P. D.	Amp.	Amp. Hrs.	Time	P. D.	Amp.	Amp. Hrs.
1.53	1.447	41.4	0	9	1.734	33.5	243
2.24	1.575	37.4	20.4	9.30	1.738	33 6	260
2.35	1.585	36.8	27.2	10	1.743	33.4	276
3	1.626	35.4	44.0	10.30	1.748	33.4	293
3.30	1 656	34.4	61.5	11	1.748	33 2	310
4	1.698	33.4	78.4	11.30	1.769	32.9	326
4.30	1.738	33.1	95.0	12	1.770	32.6	343
5	1.754	32.7	112	12.30	1.779	32.4	359
5.30	1 754	32.7	128	1	1.790	32 3	375
6	1.749	32.7	144	1.30	1.796	31.9	391
6.30	1.749	32.6	161	2	1.807	31.8	407
7	1.743	32.6	177	2.30	1 810	31.6	423
7.30	1.738	32.6	193	3	1 810	31.4	439
8	1.738	32.6	209	3.30	1.812	31.4	454
8.30	1.734	33.6	226				

TABLE III.

Charge No. 2.

Cell No. 1.				Cell No. 2.			
Time	P. D.	Amp.	Amp. Hrs.	Time	P. D.	Amp.	Amp. Hrs.
2.14	Circuit closed.			2.14	Circuit closed.		
2.16	1.718	33.0	1.10	2 20	1.713	31.0	3 10
2.45	1.733	31.5	16 7	2.45	1.755	31.5	16.1
3.15	1.728	31.8	32.5	3.15	1.733	31.8	32.0
3.50	1.712	31.9	51 1	3 50	1.718	31.9	50.5
4.15	1.708	32.0	64.4	4.15	1.708	32.0	63.9
4.45	1.698	31.6	80.3	4 47	1.695	31 6	80.8
5.15	1.700	31.4	96 1	5.17	1.708	31.2	96 5
5.21	Circuit broken.		99.2	5.21	Circuit broken.		98.6

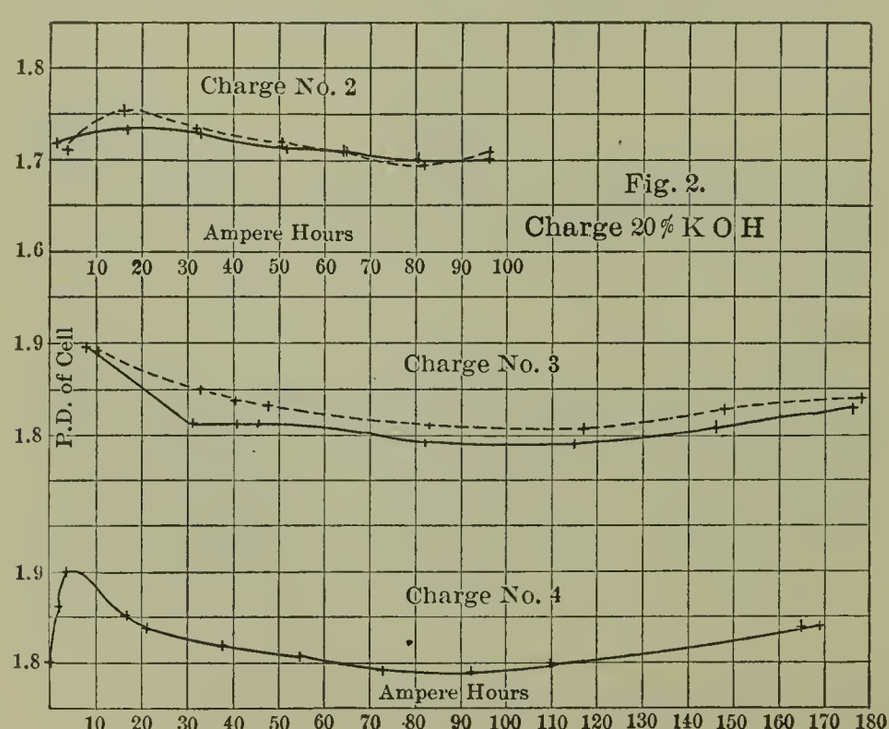


Fig. 2.
Charge 20% K O H

TABLE IV.

CHARGE NO. 3.

Cell No. 1.				Cell No. 2.			
Time	P. D.	Amp.	Amp. Hrs.	Time	P. D.	Amp.	Amp. Hrs.
3 24	. . .	71.3	Charge started.	3.24	. . .	71.3	Charge started.
3.31	1.890	65.4	7.97	3.33	1.890	65.2	10.3
3.52	1.820	68.9	31.5	3.53	1.848	68.9	32.6
4.00	1.812	68.6	40.6	4.00	1.837	68.6	40.6
4.04	1.810	69.6	45.2	4.06	1.831	69.1	47.5
4.36	1.791	68.5	82.0	4.37	1.810	68.0	82.9
5.06	1.790	63.6	115	5.08	1.811	64.2	117
5.36	1.809	60.0	146	5.38	1.829	59.7	148
6.06	1.832	61.4	176	6.07	1.849	61.4	178
6 09	. . .	. . .	179	6.09	. . .	. . .	180

TABLE V.

CHARGE NO. 4—CELL NO. 1.

Time	P. D.	Amp.	Amp. Hrs.	Time	P. D.	Amp.	Amp. Hrs.
10.20	0.746	0	0	11.15	1.816	68.9	37.5
10.42	1.800	71.3	0	11.30	1.806	68.9	54.7
10.43	1.860	65.4	1.14	11.46	1.792	68.1	73.0
10.45	1.900	65.0	3.31	12.03	1.789	68.1	92.3
10.57	1.850	68.8	16.7	1.09	1.839	64.7	165
11.01	1.836	69.6	21.3	1.12	1.839	64.7	169

TABLE VI.

DISCHARGE NO. 1—CELL NO. 1.

Time	P. D.	Amp.	Amp. Hrs.	Bridge Pot.		Absolute Pot.		Cell Calculated
				Ni	Fe	Ni	Fe	
4.15	1.285	59.2	0	0.29 c	0.96 a	—0.85	+0.40	1.25
4.30	1.213	55.2	14.3	0.25 c	0.95 a	—0.81	+0.39	1.20
5	1.193	54.3	41.7	0.25 c	0.94 a	—0.81	+0.38	1.19
5.30	1.172	53.3	68.6	0.25 c	0.92 a	—0.81	+0.36	1.17
6	1.152	52.3	95.0	0.12 c	1.03 a	—0 67	+0.47	1.14
6.30	1.101	49 8	120	0.09 c	0.99 a	—0.64	+0.43	1.07
6.52	0.816	33.9	136	. . .	. . .	. . .	. . .	. .
6.57	0.706	31.4	139	0.28 a	0.97 a	—0.28	+0.41	0.69
7.05	1.306	0	. . .	0.30 c	1.01 a	—0.86	+0.45	1.31
INTERVAL OF TWO DAYS.								
11.30	1.365	0	. . .	0.19 c	1.16 a	—0.75	+0.60	1.35
11.49	0.658	9.3	0	0.51 a	1.08 a	+0.05	+0.42	0.47
12	0.498	8.6	1.64	0.58 a	1.08 a	+0.02	+0.42	0.40
12.11	0.467	8.3	2.49	0.61 a	1.08 a	+0.05	+0.42	0.37
12.17	0.396	8.3	3.32	0.68 a	1.07 a	+0.12	+0.41	0.29
12.28	0.341	7.6	4.78	0.73 a	1.07 a	+0.17	+0.41	0.24
1.10	0.293	6.4	9.68	0.79 a	1.08 a	+0.23	+0.42	0.18
1.40	0.166	8.6	13.4	0.90 a	1.06 a	+0.34	+0.40	. .
1.45	0.161	7.6	14.1	0.91 a	1.07 a	+0.35	+0.41	. .

TABLE VII.

Discharge No. 1—Cell No. 2.

Time	P. D.	Amp.	Amp. Hrs.	Bridge Pot.		Absolute Pot.		Cell Computed
				Ni	Fe	Ni	Fe	
4.15	1.295	57.2	1.5	0.18 c	1.06 a	—0.74	+0.50	1.24
4.30	1.203	54.3	14.9	0.14 c	1.05 a	—0.70	+0.49	1.19
5	1.182	53.8	41.9	0.14 c	1.05 a	—0.70	+0.49	1.19
5.30	1.162	52.8	68.6	0.13 c	1.04 a	—0.69	+0.48	1.17
6	1.142	51.8	94.7	0.11 c	1.02 a	—0.67	+0.46	1.13
6.30	1.080	49.2	120.	0.07 c	1.00 a	—0.63	+0.44	1.07
6.52	0.669	33.4	135.	0.38 a	1.04 a	—0.18	+0.48	0.66
7.10	1.336	0	135.	0.15 c	1.03 a	. .	+0.47	. .
Interval of Two Days.								
11.42	1.365	0	. .	0.20 c	1.16 a	—0.76	+0.60	1.36
11.49	0.531	8.8	0.3	0.59 a	1.08 a	+0.03	+0.42	0.39
12.03	0.414	8.4	1.9	0.67 a	1.08 a	+0.11	+0.42	0.31
12.13	. . .	8.3	2.5	0.73 a	1 08 a	+0.17	+0.42	0.25
12.17	0.316	8.3	3.0	0.75 a	1.08 a	+0.19	+0.42	0.23
12.30	0.296	7.4	4.7	0.78 a	1.08 a	+0.22	+0.42	0.20
1.13	0.236	6.1	9.6	0.85 a	1.09 a	+0.29	+0.43	0.14
1.38	0.064	8.8	12.7	1.02 a	1.08 a	+0.46	+0.43	0.03
1.47	0.010	7.0	13.8	1.06 a	1.09 a	+0.50	+0.43	0.07

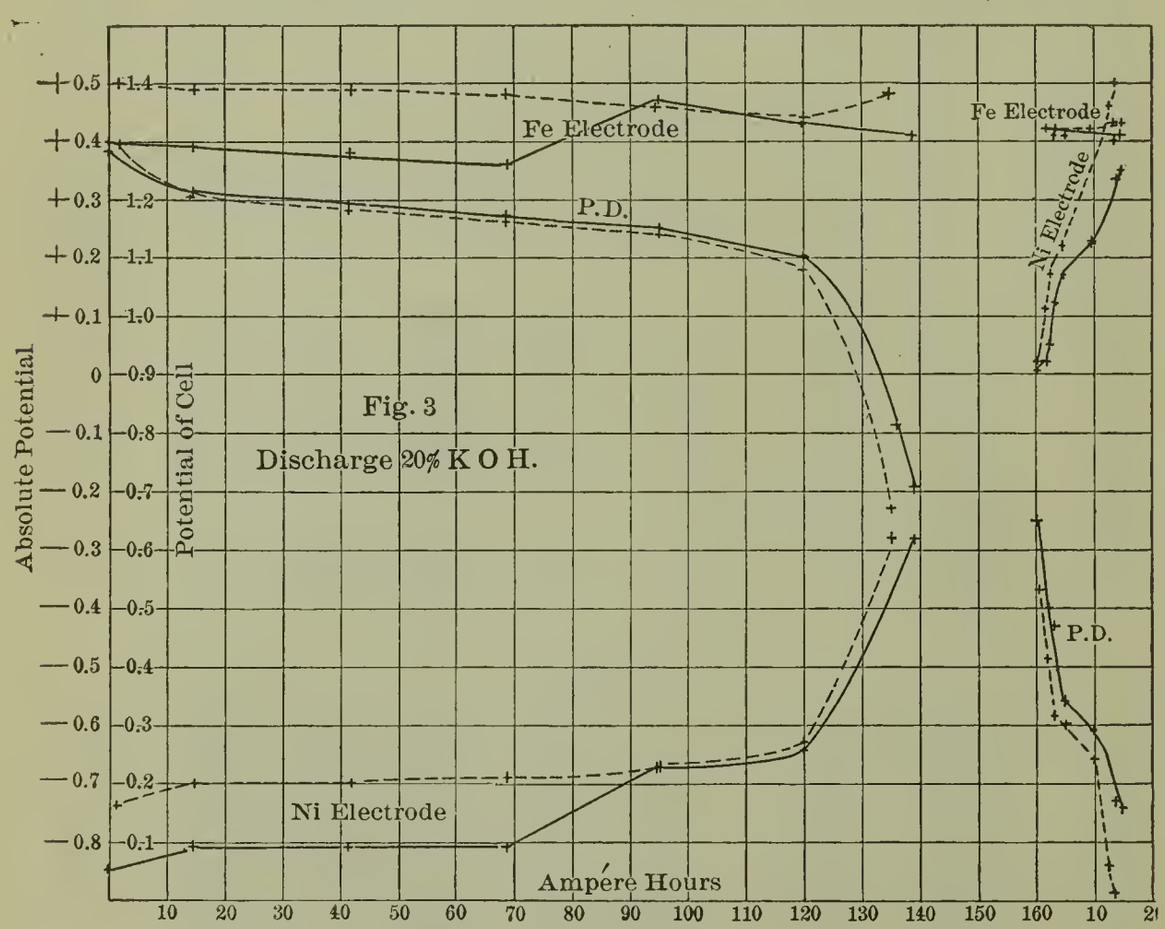


Fig. 3

Discharge 20% K O H.

TABLE VIII.

DISCHARGE NO. 2—CELL NO. 1.

Time	P. D.	Amp.	Amp. Hrs.	Bridge Pot.		Absolute Pot.		Cell Calculated
				Ni	Fe	Ni	Fe	
1.16	1.427	0	0	0.23 c	1.19 a	—0.79	+0.63	1.42
1.31	1.234	39.9	0	. . .	. . .	. . .	. . .	. .
1.32	1.213	39.3	0.66	0.16 c	1.05 a	—0.72	+0.49	1.21
1.40	1.195	39.7	5.29	0.15 c	1.05 a	—0 71	+0.49	1.20
1.50	1.187	39.5	12.5	0.14 c	1.04 a	—0.70	+0.48	1.68
2.05	1.181	39.2	22.4	0.14 c	1.05 a	—0.70	+0.49	1.19
2.35	1.160	39.4	42.0	0.12 c	1.04 a	—0.68	+0.48	1.16
2.59	1.048	39.3	57.8	0.02 a	1.00 a	—0 54	+0.44	0.98
3.03	0.798	26.9	60.0	0.31 a	1.04 a	—0.25	+0.48	0.73
3.09	0.728	15.5	62.1	0.37 a	1.09 a	—0.19	+0.53	0.72
3.14	0.718	15.4	63.4	0.36 a	1.09 a	—0.20	+0.53	0.73
3.24	0.710	15.2	66.0	0.37 a	. . .	—0.19	. . .	. .
3 36	0.710	15.1	69.0	. . .	. . .	. . .	. . .	. .
3.42	0.698	15.1	70.5	0.36 a	1.07 a	—0.20	+0.51	0.71
3.48	0.691	14.8	72.0	0.39 a	1.08 a	—0.17	+0.52	0.69
3.56	0.678	15.5	74.0	0.42 a	1.08 a	—0.14	+0.52	0 66
4.05	0.656	15.3	76.3	0.42 a	1.08 a	—0.14	+0.52	0.66
4.10	0.629	15.4	77.6	0.44 a	1.07 a	—0.12	+0.51	0.63
4.18	0.589	12.4	79.4	0.48 a	1.07 a	—0.08	+0.52	0.60
4.23	0.528	10.7	80.4	0.55 a	1.05 a	—0.01	+0.49	0.50
4.27	0.437	9.2	81.0	0.65 a	1.05 a	+0.09	+0.49	0.40
4.36	0.256	9.3	82.4	0.85 a	1.08 a	+0.29	+0.52	0.23
4.42	0.218	7.9	83.3	0.87 a	1.09 a	+0.31	+0.53	0.22
4.48	0.186	7.3	84.0	0.91 a	1.09 a	+0.35	+0.53	0.18
4.53	0.186	6.3	84.6	0.91 a	1.09 a	+0.35	+0.53	0.18
5.04	0.176	5.3	85.7	0.93 a	1.10 a	+0.37	+0.54	0.17
5.09	0.176	4.7	86.1	0.93 a	1.11 a	+0.37	+0.55	0.17

TABLE IX.

Discharge No. 2—Cell No. 2.

Time	P. D.	Amp.	Amp. Hrs.	Bridge Pot.		Absolute Pot.		Cell Calculated
				Ni	Fe	Ni	Fe	
1.20	1.428	0	0	0.24 c	1.19 a	—0.80	+0.63	1.43
1.31	1.336	39.6	0	. . .	. . .	. . .	. . .	. .
1.34	1.213	39.2	2.97	0.17 c	1.04 a	—0.73	+0.48	1.21
1.42	1.211	39.6	7.22	0.16 c	1.04 a	—0.72	+0.48	1.20
1.52	1.187	39.5	13.8	0.14 c	1.05 a	—0.70	+0.49	1.19
2.07	1.181	39.2	23.7	0.14 c	1.04 a	—0.70	+0 48	1.18
2.37	1.154	39.3	43.3	0.12 c	1.03 a	—0.68	+0.47	1.15
3.01	0.828	31.5	57.4	0.40 a	1.04 a	—0.16	+0.48	0 64
3.06	0.718	25.5	59.4	0 37 a	1.09 a	—0.19	+0.53	0.72
3.17	0.708	15.3	62.2	0.38 a	1.09 a	—0.18	+0.53	0.71
3.29	0.698	15.3	65.3	. . .	. . .	. . .	. . .	. .
3.36	0.690	15.1	67.0	. . .	. . .	. . .	. . .	. .
3.40	0 686	15.0	68.0	. . .	. . .	. . .	. . .	. .
3.45	0.678	14 9	69.2	0.40 a	1.08 a	—0.16	+0.52	0.68
3.57	0.642	15.4	72.2	0.43 a	1.08 a	—0.13	+0 52	0.65
4.07	0.563	14.9	74.8	0.52 a	1.08 a	—0.04	+0.52	0.56
4.12	0.406	14.4	76.0	0.69 a	1 08 a	+0.13	+0.52	0.39
4.14	0.326	13.4	76.5	0.78 a	1.08 a	+0.26	+0 52	0.26
4.16	0.254	12.4	76.9	0.84 a	1.08 a	+0.32	+0.52	0.20
4 20	0.188	11.7	77.6	0.91 a	1.09 a	+0.35	+0.53	0.18
4.25	0.174	10.1	78.5	0.94 a	1.09 a	+0.38	+0.53	0 15
4.33	0.098	8.9	80.4	1.00 a	1.10 a	+0.44	+0.54	0.10
4.40	0.056	8.4	81.4	1.05 a	1.10 a	+0.49	+0.54	0.05
4.45	0.016	7.9	82.1	1.10 a	1.10 a	+0.54	+0.54	0.0
4.50	0.00	6.8	82.7	1.11 a	1.11 a	+0.55	+0 55	0.0
5.06	. . .	5.3	84.3	1.14 a	1.14 a	+0.58	+0.55	—0.03

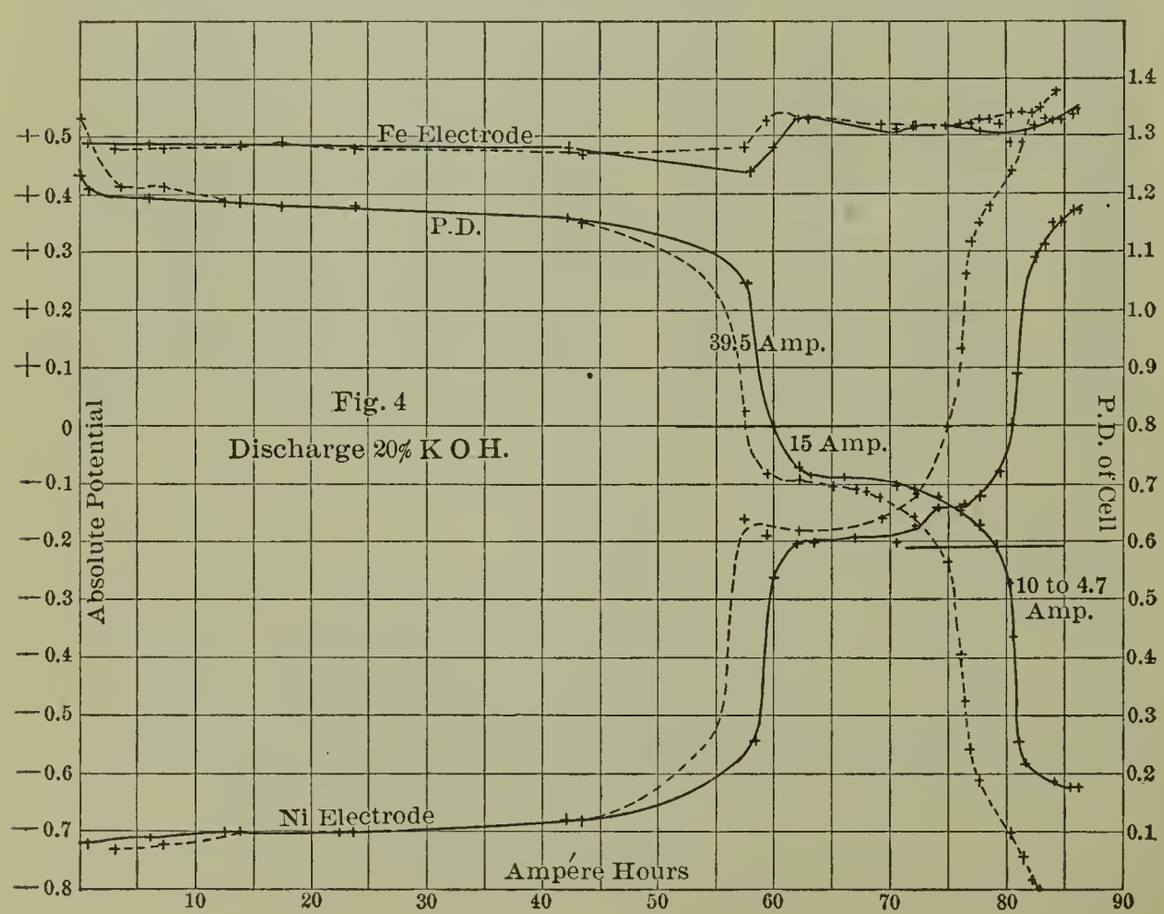


Fig. 4

Discharge 20% K O H.

TABLE X.

POTENTIALS IN 25% KOH.

Subst.	Pot.	REMARKS.
Pt wire	— .39 — .40	
Ni	— .23	Prepared by electrolyzing on Pt from Ni NO_3
Ni	—0.30	Wire from Eimer & Amend. Not c. p.
Ni	+0.46	Electrolyzed on Pt from nickel ammonium sulphate.
Ni	—0.30 —0.31	Sheet nickel, not c. p.
Graphite	—0.30	Powdered from graphite rods.
Ni_2O_3	—0.36	Mixt. of Ni_2O_3 and graphite in Pt box.
Ni_2O_3	—0.41	Mixt. of Ni_2O_3 and graphite, on Pt gauze
Ni_2O_3	—0.39	1 part Ni_2O_3 and 8 parts graphite. Made into a briquette and suspended by Pt wire.
$Ni(OH)_2$	—0.33	Mixed with graphite. Made from KOH and $NiNO_3$
Ni O	—0.43	Mixed with graphite and suspended by Pt wire.
Case	—0.20 —0.23	Pocket taken from Ni electrode.
Ni_2O_3	—0.37 —0.15	8 parts Ni_2O_3, 3 graphite, in nickel pocket.
Ni O	—0.15 —0.11	8 parts NiO, 3 graphite, in nickel case.
Fe	+ .40	Dipped in HNO_3, spc. gr. 142
Fe	+ .09	Wire gauze.
Fe	— .11	Bolt.
. . .	— .32	Rusty iron.
Fe_2O_3	—0.35 —0.31	7 parts Fe_2O_3, 3 parts graphite, in nickel case.

TABLE XI.

DISCHARGE. 50% KOH. CELL NO. 1.

Time	P. D. Volt-meter	Amp.	P. D. Measured on Bridge	Bridge Pot.		Absolute Pot.		Cell Calculated
				Ni	Fe	Ni	Fe	
0	1.499	2.00	1.512	. . .	. . .	. . .	. . .	. .
6 m.	1.326	2.00	. . .	. . .	. . .	. . .	. . .	. .
21 m.	1.203	2.00	1.206	0.09 c	1.11 a	—0.65	+0.55	1.20
27 m.	. . .	2.00	. . .	. . .	. . .	. . .	. . .	. .
36 m.	1.160	2.00	1.165	0.06 c	1.10 a	—0.62	+0.54	1.16
53 m.	1.138	2.00	1.147	. . .	1.10 a	. . .	+0.54	. .
1 h. 6 m.	1.122	2.00	1.138	0.04 c	1.09 a	—0.60	+0.53	1.13
1 h. 22 m.	1.117	1.95	1.120	0.03 c	1.08 a	—0.59	+0.52	1.11
1 h. 37 m.	1.096	2.00	1.105	0.02 c	1.08 a	—0.58	+0.52	1.10
1 h. 52 m.	1.047	2.00	1.052	0.03 a	1.07 a	—0.53	+0.51	1.04
1 h. 59 m.	0.898	2.00	. . .	. .	. . .	. . .	. . .	. .
2 h. 1 m.	0.798	2.00	. . .	. . .	. . .	. .	. . .	. .
2 h. 3 m.	0.758	2.00	. . .	. . .	. . .	. . .	. . .	. .
2 h. 5 m.	0.692	2.00	0.640	0.44 a	1.07 a	—0.12	+0.51	0.63
2 h. 21 m.	0.599	2.00	0.610	0.45 a	1.06 a	—0.11	+0.50	0.61
2 h. 31 m.	0.558	2.00	. . .	. . .	. . .	. . .	. . .	. .
2 h. 37 m.	0.488	2.00	. . .	. . .	. .	. . .	. . .	. .

TABLE XII.

DISCHARGE. 50% KOH. CELL NO. 2.

Time	P. D.	Amp.	P. D. Measured on Bridge	Bridge Pot.		Absolute Pot.		Cell Calculated
				Ni	Fe	Ni	Fe	
0	1.482	0	1.492	. . .	. . .	. . .	. . .	. .
6 m.	1.206	2.00	. . .	. . .	. . .	. . .	. . .	. .
21 m.	1.204	2.00	1.208	0.09 c	1.11 a	—0.64	+0.55	1.19
27 m.	. . .	2.00	. . .	. . .	. . .	. .	. . .	. .
36 m.	1.163	2.00	1.170	0.06 c	1.10 a	—0.62	+0.54	1.16
53 m.	1.144	2.00	1.152	0.05 c	1.10 a	—0.61	+0.54	1.15
1 h. 6 m.	1.139	2.00	1.145	0.05 c	1.09 a	—0.61	+0.53	1.14
1 h. 22 m.	1.121	1.95	1.130	0.04 c	1.09 a	—0.60	+0.53	1.13
1 h. 37 m.	1.103	2.00	1.112	0.02 c	1.09 a	—0 58	+0.53	1.11
1 h. 52 m.	1.060	2.00	1.056	0.06 a	1.11 a	—0.50	+0.55	1.05
1 h. 59 m.	0.908	2.00	. . .	. . .	. . .	. . .	. . .	. .
2 h. 1 m.	0.738	2.00	. . .	. . .	. . .	. . .	. . .	. .
2 h. 3 m.	0.678	2.00	. . .	. . .	. . .	. . .	. . .	. .
2 h. 5 m.	0.639	2.00	0.674	0.42 a	1.08 a	—0.14	+0.52	0.66
2 h. 21 m.	0.609	2.00	0.618	0.44 a	1.06 a	—0.12	+0.51	0.63
2 h. 31 m.	0.569	2.00	. . .	. . .	. . .	. . .	. . .	. .
2 h. 37 m.	0.488	2.00	. . .	. . .	. . .	. . .	. . .	. .

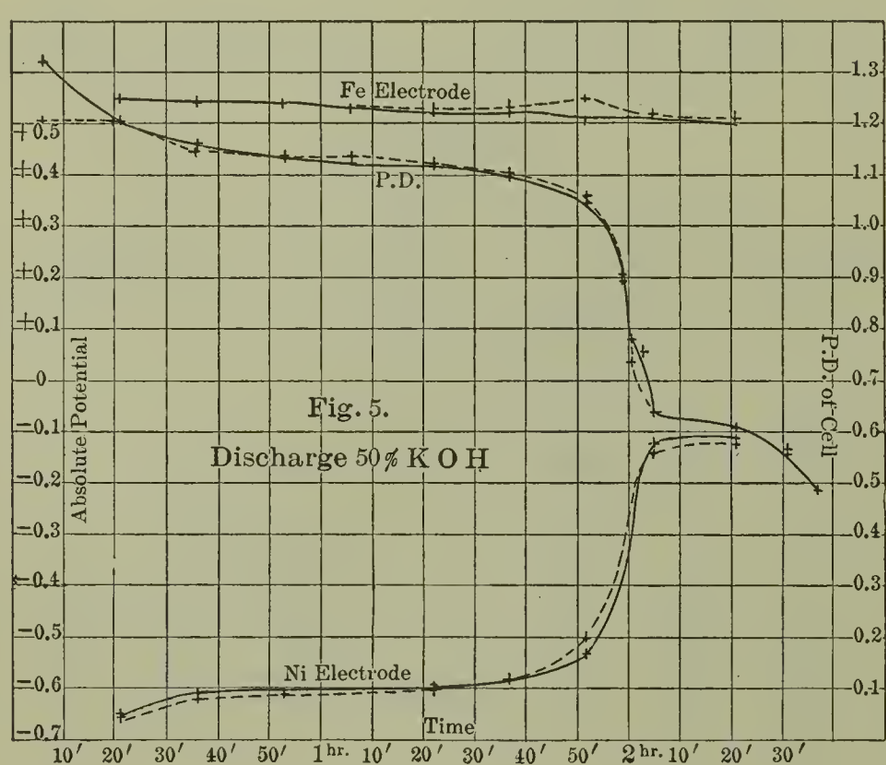


Fig. 5.
Discharge 50% K O H

TABLE XIII.

DISCHARGE. 25% KOH. CELL No. 1.

Time	P. D. Voltmeter	Amp.	P. D. Measured on Bridge	Bridge Pot.		Absolute Pot.		Cell Calculated
				Ni	Fe	Ni	Fe	
0	1.482	Open	1.493	0.26 c	1.24 a	—0.82	+0.68	1.50
6 m.	1.306	2.50	. .	. . .	. . .	. . .	. .	. .
10 m.	1.285	2.00	1.295	0.17 c	1.12 a	—0.73	+0.56	1.29
27 m.	1.221	2.00	. .	. . .	. . .	. . .	. . .	
32 m.	1.211	2.00	1.214	0.14 c	1.08 a	—0.70	+0.52	1.22
55 m.	1.182	2.00	1.184	0.11 c	1.06 a	—0.67	+0.50	1.17
1 h. 17 m.	1.162	2.00	1.170	0.10 c	1.06 a	—0.66	+0.50	1.16
1 h. 45 m.	1.142	2.00	1.153	0.09 c	1.06 a	—0.65	+0.50	1.15
2 h. 10 m.	1.123	2.00	1.136	0.08 c	1.05 a	—0.64	+0.49	1.13
2 h. 25 m.	1.108	2.00	1.118	0.06 c	1.05 a	—0.62	+0.49	1.11
2 h. 32 m.	1.084	2.00	. . .	. . .	. . .	. . .	. . .	. .
2 h. 37 m.	0.998	2.00	. . .	. . .	. . .	. . .	. . .	. .
2 h. 39 m.	0.918	2.00	. . .	. . .	. . .	. . .	. . .	. .
2 h. 40 m.	0.718	2.00	. . .	. . .	. .	. . .	. . .	. .
2 h. 42 m.	0.568	2.00	0.574	0.47 a	1.05 a	+0.09	+0.49	0.58
2 h. 43 m.	0.568	2.00	. . .	. . .	. . .	. . .	. . .	. .
2 h. 54 m.	0.568	2.00	. . .	. . .	. . .	. . .	. . .	. .
2 h. 55 m.	0.563	2.00	. . .	. . .	. . .	. . .	. . .	. .

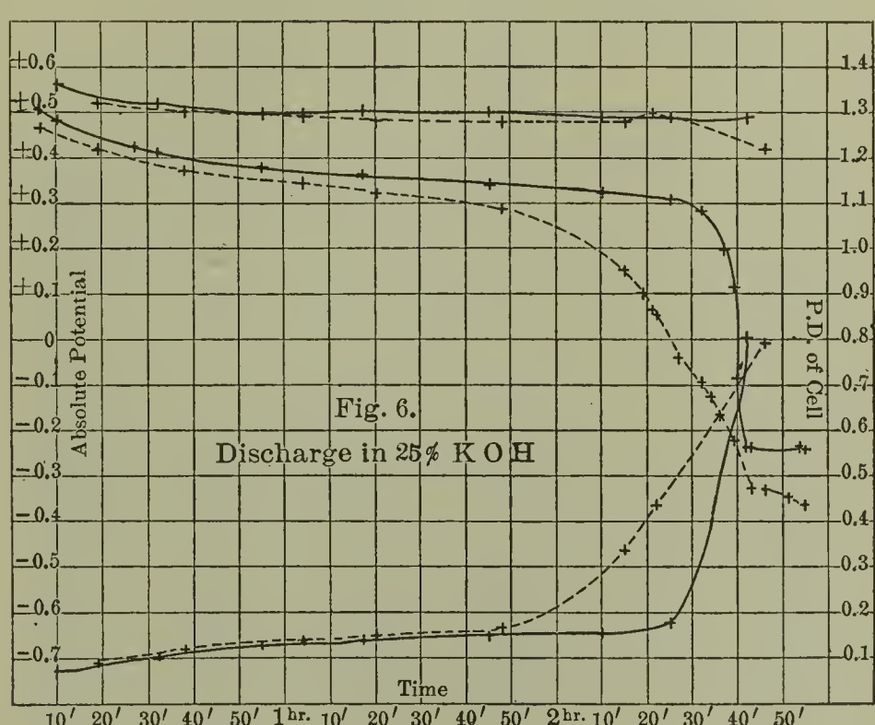


Fig. 6.
Discharge in 25% KOH

TABLE XIV.

DISCHARGE. 25% KOH. CELL No. 2.

Time	P. D. Voltmeter	Amp.	P. D. Measured on Bridge	Bridge Pot.		Absolute Pot.		Cell Calculated
				Ni	Fe	Ni	Fe	
0	1.483	Open	1.492	0.25 c	1.25 a	—0.81	+0.69	1.50
6 m.	1.269	2.50	. .	. . .	. .	. . .	. . .	. .
19 m.	1.219	2.00	1.226	0.15 c	1.08 a	—0.71	+0.52	1.23
38 m.	1.170	2.00	1.178	0.12 c	1.06 a	—0.68	+0.50	1.18
1 h. 4 m.	1.142	2.00	1.148	0.10 c	1.05 a	—0.66	+0.49	1.15
1 h. 20 m.	1.123	2.00	1.133	0 09 c	1.04 a	—0.65	+0.48	1.13
1 h. 48 m.	1.088	2.00	1.100	0.07 c	1.04 a	—0.63	+0.48	1.11
2 h. 15 m.	0.955	2.00	0.958	0.10 a	1.04 a	—0.46	+0.48	0.94
2 h. 19 m.	0.904	2.00	. . .	. . .	. . .	. . .	. . .	. .
2 h. 21 m.	0.868	2.00	. . .	. . .	. . .	. . .	. . .	. .
2 h. 22 m.	0.856	2.00	0.845	0.20 a	1.06 a	—0.36	+0.50	0.86
2 h. 27 m.	0.760	2.00	. . .	. . .	. . .	. .	. .	. .
2 h. 32 m.	0.708	2.00	. . .	. . .	. . .	. . .	. . .	. .
2 h. 34 m.	0.678	2.00	. . .	. . .	. . .	. . .	. . .	. .
2 h. 36 m.	0.637	2.00	. . .	. . .	. .	. . .	. . .	. .
2 h. 39 m.	0.558	2.00	. . .	. . .	. . .	. . .	. . .	. .
2 h. 43 m.	0.478	2.00	. . .	. . .	. . .	.		
2 h. 46 m.	0.474	2.00	0.47	0.50 a	0.98 a	—0.06	+0.42	0.48
2 h. 51 m.	0.458	2.00	. . .	. . .	. . .	. . .	. . .	. .
2 h. 55 m.	0.438	2.00	. . .	. . .	. . .	. . .	. . .	. .

TABLE XV.

DISCHARGE. 12½% KOH. CELL No. 2.

Time	P. D. Voltmeter	Amp.	Bridge Pot.		Absolute Pot.		Cell Calculated
			Ni	Fe	Ni	Fe	
0	1.487	2.00	0.28 c	1.22 a	—0.84	+0.66	1.50
3 m.	1.234	2.00	. . .	. . .	. . .	. . .	. .
4 m.	1.223	2.00	. . .	. . .	. . .	. . .	. .
7 m.	1.196	2.00	0.16 c	1.04 a	—0.72	+0.48	1.20
9 m.	1.186	2.00	. . .	. . .	. .	. . .	. .
17 m.	1.149	2.00	0.12 c	9.98 a	—0.68	+0.42	1.10
30 m.	1.101	2.00	. . .	. . .	. . .	. . .	. .
40 m.	1.077	2.00	0.11 c	0.97 a	—0.67	+0.41	1.08
45 m.	1.063	2.00	0.11 c	0.96 a	—0.67	+0.40	1.07
54 m.	1.039	2.00	0.10 c	0.95 a	—0.66	+0.39	1.05
1 h. 4 m.	1.017	2.00	0.09 c	0.93 a	—0.65	+0.37	1.02
1 h. 11 m.	0.998	2 00	0.09 c	0.91 a	—0.65	+0.35	1.00
1 h. 17 m.	0.980	2.00	0.09 c	0.90 a	—0.65	+0.34	0.99
1 h. 27 m.	0.928	2.00	0.08 c	0.85 a	—0.64	+0.29	0 93
1 h. 33 m.	0.878	2.00	0.05 c	0.83 a	—0.61	+0.27	0.88
1 h. 38 m.	0.798	2 00	0 13 a	0.89 a	—0.43	+0.33	0.76
1 h. 43 m.	0.698	2.00	0.25 a	0.94 a	—0.31	+0.38	0.69
1 h. 46 m.	0.638	2 00	. . .	. . .	. . .	. . .	. .
1 h. 51 m.	0 467	2.00	. . .	. . .	. . .	. . .	. .
1 h. 52 m.	0.406	2.00	. . .	. . .	. . .	. . .	. .
1 h. 53 m.	0.336	2.00	. . .	. . .	. . .	. . .	. .
1 h. 54 m.	0.297	2.00	. . .	. . .	. . .	. . .	. .
1 h. 56 m.	0.286	2.00	. . .	. . .	. .	. . .	. .
1 h. 57 m.	0.278	2.00	0.53 a	0.81 a	—0.03	+0.25	0.28

TABLE XVI.

DISCHARGE. 12½% KOH. CELL NO. 1.

Time	P. D. Volt-meter	Amp.	Bridge Pot.		Absolute Pot.		Cell Calculated
			Ni	Fe	Ni	Fe	
0	1.489	Open	0.30 c	1.21 a	—0.86	+0.65	1.51
2 m.	1.378	2.00	. . .	. . .	. . .	. . .	. .
4 m.	1.254	2.00	. . .	. . .	. . .	. . .	. .
5 m.	1.246	2.00	0.18 c	1.06 a	—0 74	+0.50	1.24
8 m.	1.222	2.00	. . .	. . .	. . .	. . .	. .
16 m.	1.182	2.00	. . .	. . .	. . .	. . .	
28 m.	1.142	1.91	0.14 c	1.01 a	—0.70	+0.45	1.15
38 m.	1.125	2.00	0.13 c	1.00 a	—0.69	+0.44	1.13
43 m.	1.120	2.00	0.12 c	1.00 a	—0.68	+0.44	1.12
53 m.	1.104	2.00	0.12 c	0.99 a	—0.68	+0.43	1.11
1 h. 3 m.	1.093	2.00	0.11 c	0.99 a	—0.67	+0.43	1.10
1 h. 8 m.	1.079	2.00	0.10 c	0.98 a	—0.66	+0.42	1.08
1 h. 28 m.	1.061	2.00	0.09 c	0.98 a	—0.65	+0.42	1.07
1 h. 40 m.	1.037	2.00	0.06 c	0.98 a	—0.62	+0.42	1.04
1 h. 45 m.	0.998	2.00	0.00	1.01 a	—0.56	+0.45	1.01
1 h. 47 m.	0.928	2.00	0.10 a	1.01 a	—0.46	+0.45	0.91
1 h. 49 m.	0.825	2.00	. . .	. . .	. . .	. . .	. .
1 h. 50 m.	0.778	2.00	. . .	. . .	. . .	. . .	. .
1 h. 52 m.	0.586	2.00	0.43 a	1.01 a	—0.13	+0.45	0.58
1 h. 54 m.	0.498	2.00	. . .	. . .	. . .	. . .	. .
1 h. 55 m.	0.457	2.00	. . .	. . .	. . .	. . .	. .
1 h. 56 m.	0.437	2.00	. . .	. . .	. . .	. .	. .
1 h. 58 m.	0.376	2.00	0.53 a	0.96 a	—0.03	+0.40	0.43

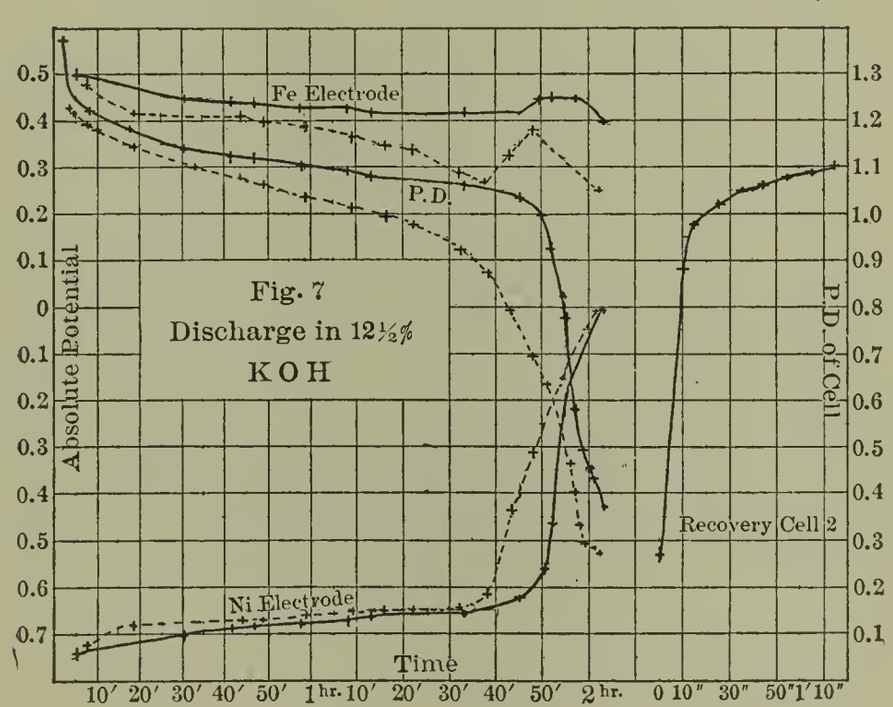


Fig. 7
Discharge in 12½%
KOH

TABLE XVII.

RECOVERY. 12½% KOH. CELL NO. 2.

Time	Volts	Time	Volts
0	0.27	45 sec.	1.06
10 sec.	0.88	55 sec.	1.08
15 sec.	0.98	1 min. 5 sec.	1.09
25 sec.	1.02	1 min. 15 sec.	1.10
35 sec.	1.05	3 min. 45 sec.	1.32

TABLE XVIII.

DISCHARGE. 6¼% KOH. CELL NO. 1.

Time	P. D. Voltmeter	Amp.	Amp. Minutes	Bridge Pot.		Absolute Pot.		Cell Calculated
				Ni	Fe	Ni	Fe	
0	1.487	Open	0	0.32 c	1.19 a	—0.88	+0.63	1.51
18 m.	1.234	2.00	0	. . .	. . .	. . .	. . .	. .
21 m.	1.142	2.00	6	0.13 c	1.01 a	—0.69	+0.45	1.14
31 m.	1.077	2.00	26	0.11 c	0.98 a	—0.67	+0.42	1.09
38 m.	1.037	1.95	39.8	0.10 c	0.94 a	—0.66	+0.38	1.04
43 m.	0.988	2.00	49 7	0.09 c	0 91 a	—0.65	+0.35	1.00
48 m.	0.945	2.00	59.7	0.09 c	0.87 a	—0.65	+0.31	0.96
54 m.	0.843	2.00	71.7	0.09 c	0.76 a	—0.65	+0.20	0.85
58 m.	0.768	2.00	79.7	0.08 c	0.70 a	—0.64	+0.14	0.78
1 h. 2 m.	0.723	2.00	87.7	0.08 c	0.65 a	—0.64	+0.09	0.73
1 h. 7 m.	0.668	2.00	97.7	0.07 c	0.60 a	—0.63	+0.04	0.67
1 h. 12 m.	0.639	1.95	108	0.07 c	0.57 a	—0.63	+0.01	0.64
1 h. 17 m.	0.561	2 00	118	0.06 c	0.49 a	—0.62	—0.07	0.55
1 h. 23 m.	0.489	2.00	130	0.08 c	0.40 a	—0.64	—0.16	0.48
1 h. 28 m.	0.386	1.62	139	0.10 c	0.28 a	—0.66	—0.28	0.38
1 h. 30 m.	0.325	1.50	142	0.11 c	0.21 a	—0.67	—0.35	0.32
1 h. 46 m.	0.226	1.28	164	0.12 c	0.11 a	—0.68	—0.45	0.23
2 h. 1 m.	0.194	1.18	182	0.11 c	0.07 a	—0.67	—0.49	0.18
2 h. 19 m.	0.056	1.02	202	0.05 a	0.08 a	—0.51	—0.48	0.03

TABLE XIX.

DISCHARGE. 6¼% KOH. CELL NO. 2.

Time	P. D. Voltmeter	Amp.	Amp. Minutes	Bridge Pot.		Absolute Pot.		Cell Calculated
				Ni	Fe	Ni	Fe	
0	1.487	Open	0	0.30 c	1.20 a	—0.86	+0.64	1.50
15 m.	1.131	2.00	0	. . .	. . .	. . .	. . .	. .
17 m.	1.121	2.00	6	0.14 c	0.98 a	—0.70	+0.42	1.12
28 m.	1.045	2.00	28	0.12 c	0.93 a	—0.68	+0.37	1.05
36 m.	0.958	2.00	44	0.11 c	0.84 a	—0.67	+0.28	0.95
41 m.	0.886	2.00	54	0.11 c	0.78 a	—0.67	+0.22	0.89
46 m.	0.798	2.00	64	0.11 c	0.69 a	—0.67	+0.13	0.80
51 m.	0.738	2.00	74	0.11 c	0.64 a	—0.67	+0.08	0.75
60 m.	0.678	2.00	92	0.10 c	0.58 a	—0.66	+0.02	0.68
1 h. 9 m.	0.642	1.90	110	0.11 c	0.54 a	—0.67	—0.02	0.65
1 h. 14 m.	0.586	2.00	119	0.11 c	0.47 a	—0.67	—0.09	0.58
1 h. 20 m.	0.518	1.80	131		. . .	. .	. . .	. .
1 h. 21 m.	0.508	1.72	133	0.13 c	0.38 a	—0.69	—0.18	0.51
1 h. 29 m.	0.464	1.40	145	0.14 c	0.33 a	—0.70	—0.23	0.47
1 h. 39 m.	0.460	1.28	159	0.14 c	0.32 a	—0.70	—0.24	0.46
1 h. 44 m.	0.457	1.25	165	0.14 c	0.32 a	—0.70	—0.24	0.46
1 h. 54 m.	0.444	1.19	177	0.14 c	0.31 a	—0.70	—0.25	0.45
2 h. 17 m.	0.519	1.00	202	0.10 c	0.43 a	—0.66	—0.13	0.53

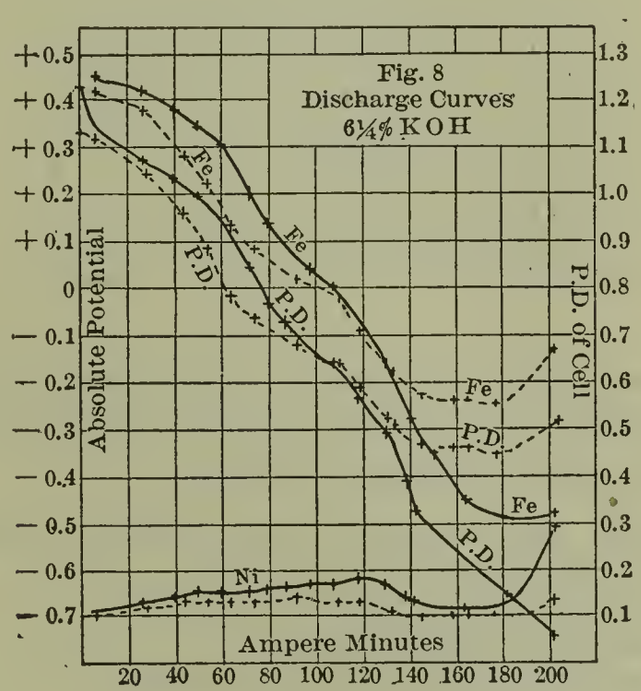


TABLE XX.

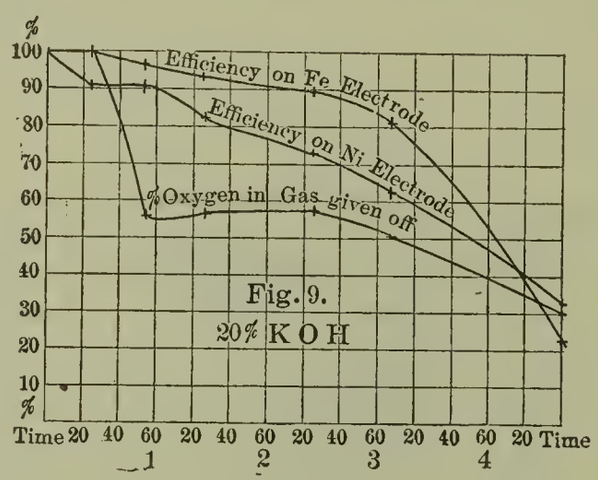
Concentration and Voltage on Open Circuit.

Concentration of KOH	Voltage	Concentration of KOH	Voltage
50 per cent.	1.49	12.5 per cent.	1.49
25 " "	1.48	10 " "	1.46
23.8 " "	1.43	6 " "	1.49

TABLE XXI.

Temperature Coefficient.

Strength of KOH Sol.	Range of Temp.	Temp. Coefficient	Strength of KOH Sol.	Range of Temp.	Temp. Coefficient
23.8 per ct.	1.3°—32.6°	+.00026	6.25 per ct.	4.6°—17.7°	+.00069
23.8 " "	4.18—20.11	+.00022	50 " "	4.9°—17.9°	+.00008



The following references include the principal publications on the Edison battery. The innumerable descriptions that have appeared from time to time are omitted.

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Hospitalier L'Industrie Électrique, Nov., 1903, p. 493.
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Joly, ibid.
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A paper read at the Seventh General Meeting of the American Electrochemical Society, held at Cambridge, Mass., April 26, 1905. President Carhart in the chair.

CHROMIUM AND THE ELECTROLYSIS OF CHROMIC ACID.

By H. R. Carveth and B. E. Curry.

(a) Unusual cathodic deposits. *(b)* Previous work on electrolysis of chromic acid. *(c)* Chemical reactions of chromic acid. *(d)* Electrochemical relations. *(e)* Preliminary electrolyses. *(f)* Experiments with pure acid. *(g)* Effect of probable impurities. *(h)* Comparison of efficiencies. *(i)* Effect of products of reaction. *(j)* Conclusions.

(a) Unusual Cathodic Deposits.—In the first paper on "Electrolytic Chromium"[1] it was remarked that a great diversity of opinion existed as to the possibility of depositing chromium from solutions of chromic acid or chromates. The selection of such a problem for investigation would by many chemists be regarded as an absolute waste of time; but a brief review of the cases where unexpected precipitations at the cathode had been observed confirmed us in the belief that the subject deserved study. The results which are presented in this paper will show that the work of a chemist which for half a century has been considered absolutely false can now, in part at least, be repeated and that a number of hopelessly contradictory statements made by different observers may be reconciled.

In dealing with the cases where the anion or a part of it is deposited at the cathode, two distinct classes of phenomena are met; in the first the element deposited is a conductor, in the second it is a non-conductor of electricity. In the case of the latter there is very little doubt that the deposition is not a primary electrolytic effect, but that it is due to chemical replacement or reaction. As illustrations may be cited the cathodic deposition of iodine, sulphur and selenium from aqueous solutions of their ic' acids.

[1] Carveth and Mott. Jour. Phys. Chem. 9, 231 (1905).

The fused or aqueous alkaline salts of the following elements have served as electrolytes from which have been obtained the conducting metals—lead, tin, zinc, tellurium, arsenic, silicon, molybdenum, tungsten, uranium, ruthenum and osmium. In these cases the metal is supposed to exist in the solution mainly as part of the anion; nevertheless, to explain conductivity and other results, the assumption has to be made that metallic cations are also present in the solution. The electrodeposition of the metal from such solutions is effected only when a definite electromotive force has been reached. Two explanations of this fact are given: The first is that the deposition from the solution is not necessarily electrolytic, but is more probably chemical, being caused by the reaction between the hydrogen or alkali metal and the electrolyte; the second regards the deposition as primarily electrolytic, but since the relative number of cations of the element may be very small, the efficiency may be very low.

Does chromium in the chromates exist as part of the anion or part of the cation? Hittorf and Lenz[2] have measured the relative velocity *n* of the cation in potassium chromate, and have found for dilution $v = 1.85$, $n = 0.448(H)$; for $v = 2$, $n = 0.49(L)$; for $v = 4$, $n = 0.53(L)$; for potassium bichromate at $v = 4.3$, $n = 0.498(H)$.

Walden[3] has found the following values for the molecular conductivity (u) of the various chromates at the dilutions named (v).

	$0.5K_2CrO_4$	$0.5K_2Cr_2O_7$	$0.5K_2Cr_3O_{10}$	H_2CrO_4
v	μ	μ	μ	μ
32	121.2	114.4	275.4	354.5
64	127.5	116.6	283.0	358.2
128	132.1	117.5	285.9	360.6
256	136.0	118.0	286.0	360.1
512	138.4	118.6	283.4	358.1
1,024	140.5	120.8	278.2	354.2

Ostwald[4] pointed out that chromic acid is weaker than carbonic, that it gives very small depressions of the freezing-point, and that its salts are of the type $M_2Cr_2O_7$; these reasons, combined with the results of Walden, have caused him to ascribe to

[2] Ostwald, Lehrbuch *2*, 1, 607.
[3] Zeit. phys. Chem. *2*, 71 (1888).
[4] Zeit. phys. Chem. *2*, 78 (1888).

chromic acid in solution the formula $H_2Cr_2O_7$. In direct opposition to Ostwald, Abegg and Cox[5] consider that in a bichromate solution there are present few Cr_2O_7 ions, and that the ions are formed from the monochromate, which being a weak acid hydrolyses; *also that CrO_3 exists free in the solution.* The greater conductivity of the monochromates as compared with the bichromates which hold the same amount of alkali they explained by assuming that the chromate ion moves more rapidly than the bichromate ion, and that in the case of the monochromate the hydroxyl ion produced in the hydrolysis increases the conductivity. The first assumption is not in accord with the results of Hittorf and Lenz as recorded above.

Connected with the study of constitution is the heat of neutralization. Thomsen found that when chromic acid was neutralized by one, two or four molecules of sodium hydrate, there was a heat evolution of 13,100, 24,700, 25,200 calories, whereas for sulphuric acid similar experiments gave 14,600, 31,000 and 31,000 calories. On the other hand, chromic acid when treated with a stronger acid, such as hydrochloric, forms a chromic salt; in solution, therefore, it should be ionized the same way as other weak bases.

Is the evidence as thus summed up absolutely conclusive that the constitution of chromic acid in solution is well known, that the chromium always exists as part of the anion, and that at no time the CrO_3 dissociates to form hexavalent chromium cations?

(b) Previous Work on the Electrolysis of Chromic Acid.—Since the anodic oxidation of chromic salts to chromates is a work of commercial importance, considerable work has been done upon it; in regard to the reactions at the cathode, the statements made are very unsatisfactory. The first one to undertake the electrolysis of the acid seems to have been Geuther.[6] His electrolyzing vessel was provided with sealed-in platinum electrodes; working with a current from four Bunsen elements, he examined the gas evolution at the electrodes and the amount of the metal deposited, while the concentration of the solutions was varied. He was able to weigh the chromium which he obtained. One set of his results is given in Table I. The I which he thought he was using in prac-

[5] Zeit. phys. Chem. *48*, 725 (1904).
[6] Liebig's Ann. *99*, 314 (1856).

tically the tenth part of an ampere, since calculation (Table I) indicates that 0.7801 I for 1,177 seconds produces 7,650 mgms. of oxygen, or that 8 grams would require 96,017 coulombs. Working on the assumption that 96,540 coulombs will deposit 8 grams of oxygen, we have added the last column in order to determine the efficiencies. The nomenclature is that used by Geuther. In the table the numbers refer to his experiment; the solution used is then given; I refers to the current intensity (approximately tenths of amperes); D to the time in seconds; Cr. to the weight in milligrams of the chromium found; O_{vol} to the volume in cc. of oxygen in the electrolyzing vessel reduced to 0° and 760 mm, and O to the weight in milligrams of this gas; O_I to the calculated weight of oxygen which should have been evolved by the current; H_{vol} to the volume in cc. of hydrogen in the electrolyzing vessel reduced to 0° and 760 mm., and H to the weight of this gas; H_I to the weight of hydrogen corresponding to the current passed. The percentage of hydrogen deficiency computed from the hydrogen columns (the deposition of the metal being ignored) is given in the H_D column. The last column gives the number of grams of chromium which would be deposited by 96,540 coulombs.

TABLE I.

		I	D	Cr.	O_{vol}	O	O_I	H_{vol}	H	H_I	H_D	Cr.
		Current Tenth Amperes	Seconds	Mgms.	Volume Cell Oxygen	Weight Cell Oxygen	Weight Voltameter Oxygen	Volume Cell Hydrogen	Weight Cell Hydrogen	Weight Voltameter Hydrogen	Hydrogen Deficiency	Grams per 96,540 Coulombs
1	4.76%, new . . .	0.780	1177	3.00	8.614	12.320	7.650	8.214	0.7343	0.9566	23.24	3.13
2	4.76%, used in I . .	0.780	881	2.20	6.621	9.470	5.728	6.128	0.5478	0.7161	23.50	3.07
3	9.09%, new . . .	1.822	1136	9.00	17.583	25.150	17.250	10.246	0.91 9	2.1566	57.53	4.17
4	9.09%, partly renewed	1.909	891	7.00	13.620	19.480	14.180	9.149	0.8178	1.7722	53.85	3.94
5	Residue from IV	1.909	776	6.00	12.216	17.473	12.345	8.520	0.7616	1.5435	50.65	3.88
6	14.28%, new . . .	3.526	696	10.50	17.586	25.153	20.455	9.922	0.8869	2.5568	65.48	4.10
7	Used in VI . . .	3.307	660	9.20	17 586	25.153	18.189	9.940	0.8885	2.2736	60.53	4.04

The current densities employed must have been very great, since platinum wires were used; but for solutions of practically the

same concentration, this may have been maintained sufficiently constant. Other results obtained by Geuther indicated that at the anode, *more* oxygent was evolved than corresponded to the Faraday Law. This is indicated in the following table, the numbering of the original article being retained; the numbers in the first column refer to the solutions of Table I. The last column is our own addition to Geuther's table.

TABLE II.

	I	D	O_{VOL}	O	O_I	O÷ID	Excess	Excess
Solution	Current Tenths of Amp.	Seconds	Volume Cell Oxygen	Weight Cell Oxygen	Weight Volt-ameter Oxygen	Mgms. Oxygen per Coulomb	Oxygen in Mgms.	Percent. of Oxygen
3	1.822	282	3.796	5.418	4.283	0.01056	1.135	29.9
	.....	579	8.329	11.913	8.793	0.01129	3.210	38.53
	.....	1,017	15.250	21.810	15.440	0.01177	6.370	41.78
	.....	1,136	17.583	25.150	17.250	0.01215	7.900	44.92
4	1.909	271	3.797	5.431	4.312	0.01050	1.119	29.47
	.....	570	8.330	11.914	9.070	0.01095	2.844	34.15
	.....	891	13.620	19.480	14.180	0.01145	5.300	38.91
5	1.909	264	3.813	5.453	4.201	0.01097	1.252	32.60
	.....	567	8.365	11.965	9.022	0.01105	2.942	35.18
	.....	776	12.216	17.473	12.345	0.01179	5.128	42.00
6	3.526	172	3.799	5.435	5.055	0.00896	0.380	10.00
	.....	355	8.338	11.925	10.433	0.00953	1.492	17.89
	.....	477	11.780	16.848	14.020	0.01002	2.828	24.01
	.....	696	17.586	25.153	20.455	0.01025	4.698	27.98
7	3.307	163	3.799	5.435	4.492	0.01008	0.943	24.26
	.....	337	8.338	11.925	9.287	0.01070	2.638	31.63
	.....	454	17.780	16.848	12.512	0.01122	4.336	24.38
	.....	660	17.586	25.153	18.189	0.01152	6.964	39.61

Some other results obtained by Geuther are to be noted. He states that the amount of metal deposited seems to reach a maximum when the solution contains one part of chromic acid to ten parts of water; also that the amount of metal deposited diminishes as the current is passed. The more concentrated the solutions the greater is the reduction; the further the electrolysis has been carried, the less is the reduction. The amount of chromium deposited stands in direct relation to the hydrogen deficiency.

The theoretical views expressed by Geuther (combined with the novelty of his results) caused Buff[7] to undertake the electrolysis of chromic acid. The electrolysis was performed in a small vessel into which platinum wires were sealed; the gases were collected in U tubes. Four Bunsen elements supplied the current. With a 5.13 per cent. acid solution he performed experiments which are recorded in Table III. In the last two experiments sulphuric acid was added.

TABLE III.

	Time Min.	Degrees Tan. Galv.	C.c.O Evolved	C.c.H Evolved	C.c.H in Volta-meter	Percent. H Evolved	Electrodes
1	20	1.5	25.4	19.0	51.5	36.9	Platinum wires
2	6	7.9	35.3	32.5	73.6	44.1	" "
3	6	7.55	35.1	7.4	70.0	10.5	1.5 x 1 inch
4	5	6.8	....	2.2	50.8	4.3	"
5	4	9.65	....	7.2	62.0	16.1	"
6	4	9.4	....	0.6	57.2	1.0	"
7	5	12.8	....	1.6	61.2	2.6	"

Buff was successful neither in obtaining a deposit of metallic chromium nor in noting an excess of oxygen at the anode. He therefore claimed that the results of Geuther were unreliable, basing this on the criticism that the galvanometer used by the latter had not been calibrated against the hydrogen voltameter, whereas Buff's results were obtained with the gas voltameter. The reply of Geuther[8] does not insist upon the reliability of his experimental work. He states: "Was die Electrolyse der Chromsäure betrifft, so hat Buff gezeigt dass sich bei meinem Messungen der Stromintensität, welche mit einer Tangenten boussole ausgeführt werden, deren Magnetnadel wohl nicht die zu diesen Messungen erforderliche Empfindlichkeit besessen haben mag, ein Irrthum eingeschlossen haben müsse. Dadurch wurden allerdings *die* Gründe beweislos, welche aus den Messungen abgeleitet worden waren, nicht aber die anderen dort angeführten." The subject seemed closed to discussion by a second paper from Buff[9] and the complete experimental work of Geuther utterly discredited.[10]

[7] Liebig's Ann. *101*, 1 (1857).
[8] Liebig's Ann. *109*, 129 (1858).
[9] Liebig's Ann. *110*, 278 (1858).
[10] Le Blanc, Darstellung des Chroms, p. 91.

In 1878 Morges[11] stated that chromic acid in dilute solution was reduced to chromium chromate by the current. Bartoli and Papasogli[12] electrolyzed the acid, making use of graphite electrodes. Again the statement was made that metallic chromium was obtained.

In 1894 Placet and Bonnet were granted an American patent,[13] the specifications of which are in all probability more complete than those of their earlier European patents. They state that of the electrolytes which they use, "the most important of these compounds is chromic acid, either the *commercial* acid or chromic acid obtained from chromate or bichromate of an alkali metal." They also patented the use of most of the soluble chromic salts. To vary the shade of the metal they added small amounts of other acids. The concentrations of the electrolytes used are given, but the only clue to the other experimental conditions which they may have used is indicated in another of their patents[14] where high current densities are suggested. Their statement is: "By increasing the pressure an electric current may be passed having an illimitable power. Under these conditions a composite body does not exist which may not be decomposed." As to the yields, the American Patent states: "By our processes, as hereinafter set forth, we obtain electrodeposited chromium of great purity in coherent masses of sufficient size for various industrial uses, and of various colors, as may be desired. In these processes we use salts and compounds of chromium which heretofore have never been used or proposed for use for the purpose in view, and from which in the manner hereinafter pointed out, metallic chromium is produced in sufficient quantity and with sufficient economy to constitute an industrial process, very different from the result of laboratory experiments by which the production of minute specimens of metallic chromium has been hitherto attempted."

In his monograph on chromium Le Blanc[15] devotes many pages to a review of the patents of Placet and Bonnet, and finally in conclusion states that either the metal cannot be obtained in the way indicated in the patents or that at least all of the necessary

[11] Comptes rendus, *87* 15 (1878); compare also Favre, Ibd. *73*, 890, 936 (1871).
[12] Gazz. chim. Ital. *13*, 47 (1883).
[13] U. S. Patent 526,114, Sept. 18 (1894).
[14] English Patent 19.344 (1890).
[15] Darstellung des Chroms, pp. 3-17.

conditions are not there given in detail.[16] He cites the fact that Cowper Coles, Ferée and Schick had been unsuccessful in their attempts to reproduce the conditions indicated in the patents. In the Jahrbuch der Electrochemie, I, 174, the criticism of the Placet-Bonnet patent is "Nach der erwähnten Vorschriften ist aber eine Fabrication nie möglich." Ahrens[17] states, "Die Patentschrift ist indessen so abgefasst dass auf dem darin angegebenen Wege, Chrom unmöglich fabriziert werden kann."

In 1899 Reese[18] electrolyzed chromic acid, examining the effect produced on the electrolyte by the gases evolved. As an electrolyzing vessel he used a burette; the cathode was put at the bottom so that the rising hydrogen passed through a long column of the acid. With pure acid of normal concentration he found no reduction even after an electrolysis of 24 hours; when, however, traces of sulphate or sulphuric acid were present, reduction was quickly effected, "but there was always a limit reached when no further reduction took place." Potassium bichromate behaved in exactly the same way as the acid. Neither the current density employed nor other important experimental details are given. The results, however, might at first sight seem to be in direct opposition to those obtained by Geuther and Buff, both of whom found considerable reduction.

This historical review raises several questions: (1) May metallic chromium be deposited in the electrolysis of chromic acid solutions? (2) If so, under what conditions and what is the current yield? (3) Why is there such a great diversity of experimental results and conclusions? (4) Is there reduction at the cathode or oxidation at the anode? (5) Is the statement of Geuther in regard to the excess of oxygen at the anode correct?

(c) Chemical Reactions of Chromic Acid.—In every electrochemical study an accurate knowledge of the oxidation and reduction possibilities of the compounds involved is necessary. This is especially needed in the case of the compounds which are considered in this paper.

Chromic acid is a very powerful oxidizer, or, in other words, it is very easily reduced; in fact, even hydrogen[19] will effect the

[16] Compare Jour. Phys. Chem. *9*, 235 (1905).
[17] Handbuch der Electrochemie, p. 442.
[18] Am. Chem. Jour. *22*, 162 (1899).
[19] Ludwig, Liebig's Ann. *162*, 47 (1872).

reduction of saturated solutions. Catalytic agents such as platinum would probably accelerate this reduction. The more pure the acid the less readily is it reduced. This is shown by the work of Gawalovski,[20] who found that the pure acid reacts with alcohol very slowly, but that the addition of an acid accelerated the reaction very decidedly. This is another confirmation of the results of Bancroft, who showed that the addition of an acid raised the potential of an oxidizer. Another illustration of this principle where chromic acid is again involved is the Grove cell, where zinc and graphite electrodes are used in a mixture of sulphuric and chromic acid. With the low current density at which the cell is used, the acidified chromic acid acts as an almost ideal depolarizer, since by the addition of the sulphuric acid its oxidation potential has been very much increased; the result is the formation of chromic sulphate as the cell is discharged.

The reverse operation—the oxidation of chromic salts to chromates—may be effected by the use of oxidizers, such as manganese or lead peroxide, potassium permanganate or chlorine in acid solutions.

(d) Electrochemical Relations.—Chromium is an element which shows at least three different valencies; the electrochemical relations have been worked out by Luther,[21] who gives the following values, assuming the potential —0.56 for the Ostwald normal electrode:

Potential of metallic chromium against its divalent salts = 0.3 volts.

Potential of metallic chromium against its trivalent salts = 0.2 volts.

Potential of metallic chromium against its hexavalent salts = — 0.9 volts.

The question of the potential of the metal in solutions of chromium chromate was not considered. The theoretical method employed by Luther was criticised by Hittorf,[22] on the ground that chromium in chromic acid was not a reversible electrode, since from the chromate solutions it was impossible to obtain the metal. While Luther admitted this last fact, he claimed that it did not affect the conclusions which he had drawn.

[20] Zeit. analyt. Chem. *17*, 179 (1878).
[21] Zeit. phys. Chem. *36*, 389 (1900).
[22] Zeit. Electrochem. *7*, 257 (1900).

Hittorf has shown that chromium when used as anode goes into solution with different valencies according to the conditions used. The electromotive forces involved are illustrated by the combination chromium, potassium chloride, sodium nitrate, silver nitrate, silver. When active chromium was used, Hittorf found an electromotive force of 1.006 volts, silver being cathode. This value increased as the temperature rose, finally forming a constant element. At the lower temperature the rate of solution showed the metal hexavalent, while at the higher it tended to become divalent.[23] It seems very probable, both from the work of Hittorf and from some experiments that we ourselves have made, that the changes of valency are not discontinuous, but that systematic study would show all stages of valence (anodic efficiency) lying between hexavalent and divalent.

The fact that the metal goes into solution at the anode as a hexavalent ion may be explained by the modern theory of the voltaic cell thus—the metal has a solution tension which is determined by the presence in the solution of hexavalent chromium ions. As shown above, Luther has calculated this value as —0.9 volts; nevertheless, in the inconclusive work on the constitution of chromic acid which we have quoted at the beginning of this paper, there was no mention whatever of the possibility of the presence of hexavalent chromium ions in the solution. The nearest approach to such a suggestion was made by Abegg and Cox, who claimed that free CrO_3 exists in the solution.

To explain the results of Hittorf and Luther, the assumption must therefore be made that some hexavalent chromium ions—cations—exist in the solution of chromic acid. This assumption would be given some support if proof could be adduced that chromium can be deposited from chromic acid; and while it rarely happens that a cathode reaction is the exact converse of the anode reaction, nevertheless some information as to the action of reversible electrodes should be obtained from the cathode reactions.

We pass at once, therefore, to the results obtained in the actual electrolyses of chromic acid.

[23] This is probably an illustration of a general principle that rise of temperature favors the dissolution of the anode to compounds in which the metal shows its lower valency. We may later examine the limitations of this suggestion in relation to the heat and electrical energies involved in the changes of valence.

(e) Preliminary Electrolyses.—As electrolyte there was selected a chromic acid which contained considerable sulphate as impurity. This was washed repeatedly with concentrated nitric acid and dried in an air bath at 160°. The electrodes which were used throughout the investigation were platinum wires 0.4 mm. in diameter, 30 mm. long; the area of these was approximately 0.004 square decimeters. With various concentrations of the chromic acid, we now made a series of electromotive force current measurements. For two reasons these results are not given. A very careful analysis of the acid had not been made, and hence it is impossible to reproduce the measurements, and secondly, the runs were not carried far enough to determine with exactness the exact decomposition voltages. Nevertheless, chromium deposits were obtained; the measurements gave, therefore, very rough indications as to the current densities which were necessary. For solutions ranging in concentration from one to fifty per cent. acid, the current density at which an instantaneous deposition of metal was observed was about 80 amperes per sq. dcm. at 18°, while twice this density was necessary at a temperature of 90°.

At the lower current densities hydrogen was liberated. The question was at once raised as to the absorption of this gas by the metal. Of a quantity of chromium deposited from chromic acid solution, 0.6979 grams when heated gave 24.6 cc. of hydrogen at $t = 20°$, $p = 750$ mm.; as a rough approximation then, one volume of electrolytic chromium had absorbed 250 times its volume of hydrogen. This metal shows, then, the same or perhaps even greater power for absorbing hydrogen than palladium, platinum, iron and nickel.

Chromic acid labeled "C. P., free from sulphate," was now obtained from a reputable firm. Again sulphate was found in considerable amounts. Reduction to chloride and precipitations as barium sulphate showed 0.23 per cent. of free acid. The precipitate was white and lost little weight on repeated washings with hydrochloric acid. When barium chloride was added to the chromic acid solution strongly acidified with hydrochloric acid, the percentage of sulphate found was only 0.14 per cent. However, more of the sulphate precipitated from this solution after the filtrate had stood for several days, the total percentage increas-

ing to 0.20 per cent. of sulphate acid impurity. Nitric acid was also present in minute amounts.

The solutions were electrolyzed in a well-stoppered cylinder, which was kept in a bath of constant temperature. The ammeter readings served only for a rough adjustment, since an alkaline nickel voltameter was always kept in circuit. The gases from the voltameter were analyzed repeatedly to check the accuracy of the results obtained. The cathode deposit was weighed after careful washing and drying in the air-bath. The gases evolved from the cells were collected in a Hempel burette and then analyzed for oxygen, using the alkaline pyrogallol and phosphorus absorption methods.

With temperature constant, but varying current, a run was now made, using 50 cc. of a 14.28 per cent. acid solution. This concentration was chosen in order to allow comparisons with the work of Geuther; most of the tables refer, therefore, to this strength. The results are given in Table IV, which, as in all subsequent tables, is arranged as follows: The first column gives the number of the experiment, the second the time in seconds, the third the number of cc. of gas found in the voltameter, the fourth the cc. of gas in the cell. The number of cc. of oxygen gas found in this cell is shown in the next column, while the difference between the figures in the fourth and fifth columns gives the number of cc. of hydrogen recorded in the sixth column. The percentage deficiency of hydrogen given in the seventh column is calculated on the assumption that no other decomposition had taken place. The eighth row gives the number of milligrams of the metal deposited. The last row, which is to be found only in Table IV,

TABLE IV.

14.28% acid; cylinder electrolyzer; t = 21°

No.	Seconds	Volt. Gas	Cell Gas	Cell Oxygen	Cell Hydrogen	Percent. Reduction	Mgms. Cr.	Amp.
1	3,300	80.2	76.4	26.7	49.7	6.9	0.0	0.11
2	363	84.0	71.2	28.0	43.2	22.7	7.8	1.20
3	360	83.8	....	....	....	....	8.0	1.20
4	364	87.0	72.8	29.0	43.8	26.2	9.7	1.20
5	960	84.4	67.0	28.1	38.9	30.9	10.8	0.45
6	1,020	89.0	70.0	29.6	40.4	31.9	10.8	0.45
7	271	92.2	78.0	30.7	47.3	23.1	9.9	1.70
8	259	94.5	81.4	31.5	49.9	20.8	9.1	1.95

indicates the ammeter reading. For all other tables the temperature and current were kept quite constant.

It will be noted that for a current of 0.11 amperes (area of anode and cathode in every case equals 0.004 sq. dcm.), there was a slight reduction but no deposition of metal. Increase of current density caused greater reduction and some metal deposition. Thereafter in most of the runs efficiency in reduction is practically synonymous with efficiency in metal deposition.

A run was now made to ascertain how the efficiency varied with the time of electrolysis when the temperature and current were constant. Between experiments 5 and 6, 7 and 8 electrolysis was continued for some time, during which no analyses were made. Results are given in Table V.

TABLE V.

14.28% acid; cylinder electrolyzer; current = 1.2 ampéres; t = 22° ± 2°.

No.	Seconds	Volt. Gas	Cell Gas	Cell Oxygen	Cell Hydrogen.	Percent Reduction	Mgms. Cr.
1	354	84.6	71.1	28.2	41.9	25.7	8.0
2	351	84.0	67.4	28.0	39.4	29.6	...
3	360	83.0	66.5	27.6	38.9	29.6	...
4	380	87.0	70.3	29.0	41.3	28.8	...
5	340	85.5	68.9	28.5	40.4	29.1	..
	1,800	....	....	....	....	....	..
6	362	85.8	69.4	28.6	40.8	28.6	...
	3,600	....	....	....	....	....	...
7	345	84.4	77.5	28.1	49.4	12.2	....
	4,200	....	....	....	....	....	...
8	360	87.3	82.1	29.1	53.0	8.9	...
9	382	87.2	82.8	29.0	53.8	7.2	...
10	365	83.6	79.4	27.9	51.5	7.5	2.2
11	343	82.6	79.2	27.5	51.7	6.1	2.2

The metal deposited in 1, Table V, weighed 8 milligrams; the cathode deposit was not again determined until 10 and 11, when in each case 2.2 mgms. was found. This series shows that the percentage reduction as well as the metal deposition fell off as the run was continued.

(f) Results with Pure Acid.—Reese had stated that with pure chromic acid he was unable to get any reduction whatever. We therefore obtained a chromic acid from Merck which by the Krauch test showed no impurities. Analysis showed that there was present 0.01 per cent. of free sulphuric acid and very slight

traces of nitric acid and alkali metal. While recrystallization would undoubtedly have given us an acid still more pure, it would have required the greatest care and a long time to obtain by the necessarily slow crystallization an acid much purer. The probabilities are that the acid is at least as pure as any that has been used in conductivity or electrolytic work. In all our subsequent electrolyses we have, therefore, used this acid.

When a 14 per cent. solution of this acid was electrolyzed for two days with a very low current derived from a two-volt circuit, no reduction was observed and no metal was deposited. A current-electromotive force curve showed the decomposition voltage at which metal was observed was 2.31 volts; hydrogen was evolved from 1.6 volts or even lower. The electrolyzing cell was connected to a four-volt circuit; metal deposition and darkening of the solution were noticed almost immediately when the circuit was closed. It seems very probable, therefore, that Reese used low currents for his electrolyses, and that he was below the point at which metal deposition was to be expected.

For the experiments cited in the last paragraph and in all subsequent work we have made use of a glass-stoppered glass cell in order that the possible reduction of the chromic acid by organic matter, which might come from a rubber stopper, should be completely eliminated. The cathode was fastened into a ground glass stopper which could be readily cleaned and weighed. The anode was sealed in at the bottom. The gases evolved were led through a side arm into a gas burette. The small content of the cell (3 cc.) enables one to control the temperature very readily, while another advantage is that a run may be carried to a final stage in a very short time. The small gas space over the solution also allows one to reproduce conditions with great exactness.

With this purer acid and the glass electrolyzer runs were made to find the effect of temperature; the current used, 0.5 ampere, corresponds to a density at anode and cathode of 125 amperes per square decimeter. The results obtained at 20° are given in Table VI, at 90° in Table VII.

TABLE VI.

14.28% acid; glass electrolyzer; current = 0.5 amp.;
D anode = D cathode = 125; t = 20°

No.	Seconds	Voltameter Gas	Cell Gas	Cell Oxygen	Cell Hydrogen	Percent. Reduction	Mgms. Cr.
1	960	96.2	89.8	31.9	57.9	9.8	3.6
2	960	94.5	92.8	31.0	61.8	1.9	0.9
3	780	79.5	79.5	26.7	52.9	0.2	0.4
4	960	92.4	91.0	30.8	60.2	2.2	0.7
	4,800	....	....	....	....	...	...
5	1,020	93.9	93.0	31.0	62.0	1.0	0.4

TABLE VII.

14.28% acid; current = 0.5 amp.; D anode = D cathode = 125; t = 90°.

No.	Seconds	Voltameter Gas	Cell Gas	Cell Oxygen	Cell Hydrogen	Percent. Reduction	Mgms. Cr.
1	900	90.6	90.5	30.2	60.3	0.2	0.2
2	840	90.1	89.0	29.8	59.2	1.2	0.3
	3,600	....	....	....	....	...	...
3	1,080	98.4	97.1	31.7	65.4	0.3	0.2
	1,080	....	....	....	....	...	...
4	840	97.9	96.2	32.0	64.2	1.5	0.2

It was necessary to stop the series after the fifth run (Table VI) because of the presence of a large amount of an insoluble precipitate.

It will be noticed that in the electrolysis at 20°, metal is deposited from the first and that the reduction and metal depositions decrease as the run continues. Small errors in analysis are, of course, greatly magnified when dealing with cases showing such little reduction as is here found. At the higher temperature, reduction and metal deposition are insignificant.

(g) Effect of Impurities.—Comparison of Tables IV and V with VI indicate that, as was noted in a discussion of the reactions of chromic acid, a slight amount of impurity may have a very noticeable effect on the reduction. Geuther had made his acid from potassium bichromate and sulphuric acid, while Buff and Reese made use of C.P. acid. None of the chemists who have written about the electrolysis of chromic acid have described the methods by which the pure acid may be obtained and tested. It is a long and difficult operation to free it from the sulphuric acid

used in its manufacture and the sodium sulphate which occurs as the byproduct, or the nitric acid which is used in freeing from the sulphuric. It seemed possible, then, that the deliberate addition of impurities might enable one to duplicate the results obtained, especially in the cases where the object of the work had been purely commercial and where under no circumstances could a chemically pure chromic acid have been used.

To the 14.28 per cent. chromic acid solution was added sulphuric acid in amount sufficient to make its concentration one per cent. The other conditions were the same as had been employed in Table VI, namely t = 20°, current 0.5 amperes. The results are given in Table VIII.

TABLE VIII.

14.28% chromic + 1% sulphuric; current = 0.5 amp; D anode = D cathode = 125; t = 20°

No.	Seconds	Voltameter Gas	Cell Gas	Cell Oxygen	Cell Hydrogen	Percent. Reduction	Mgms. Cr.
1	930	98.5	52.3	31.1	21.2	66.2	15.2
2	935	98.2	55.2	30.8	24.4	62.7	19.8
3	510	57.3	33.1	16.1	17.0	55.5	11.4
	3,600	....	....	....	....	....	....
4	570	71.4	43.8	21.3	22.5	52.8	6.4
	7,200	....	....	....	....	....	....
5	535	60.3	58.7	19.0	39.7	1.2	3.0

In all cases the metal deposit scaled very badly, and in some cases fell into the solution, so that the results are approximations only. A duplicate set of determinations for metal only gave the following numbers in milligrams: 19.1, 20.8, 16.2, 17.3, 0.9, 7.8, 1.9, while in the solution was 20 milligrams of scale deposit. It is at once apparent that the effect of the sulphuric acid has been to increase the reduction and the metal deposition to a very great extent. In fact, in the runs recorded in Table VIII and its duplicate, *one-half of the total chromium contents of the solution was removed as metal,* and even then the limit had not been reached. As before noted, the reduction fell off as the run was continued; neither oxygen excess nor ozone formation has been observed.

The platinum anode was now replaced by a lead anode of the same area and a run made under conditions identical with (2)

of Table VIII. As was to be expected, there was a greater deficiency of oxygen, while the reduction was only 55.4 per cent. in place of 62.7 per cent.

A solution was now made up which contained 14.28 per cent. of chromic + 1 per cent. sulphuric acid + 1 per cent. potassium sulphate. It was electrolyzed under conditions identical with those used in VI and VIII. The results are given in Table IX.

TABLE IX.

14.28% chromic + 1% sulphuric + 1% potassium sulphate; current = 0.5 amp; D anode = D cathode = 125; t = 20°

No.	Seconds	Voltameter Gas	Cell Gas	Cell Oxygen	Cell Hydrogen	Percent. Reduction	Mgms. Cr.
1	900	93.5	44.2	25.4	18.8	69.8	22.6
2	780	87.7	45.8	27.6	18.2	68.8	16.8
	4,500	....	....	....	....	....	....
3	900	90.3	85.7	27.7	58.0	3.6	0.5
	4,500	....	....	....	....	....	....
4	870	93.2	91.0	29.5	61.5	0.9	0.9
5	960	98.0	95.8	28.4	64.6	0.9	0.7

In runs 1 and 2 the metal scaled very badly; from 3 to 6 the metal was black. The first run shows great reduction, high metal deposition (at the rate of 4.6 grams metal per 96,540 coulombs) and considerable oxidation; as the run continues, the reduction and metal deposition drop off very considerably, while the oxidation efficiency decreases more slowly.

To the 14.28 per cent. acid was now added potassium chromate to make a one per cent. solution in respect to the chromate. The conditions of electrolysis remained constant. The results are given in Table X.

TABLE X.

14.28% acid + 1% potassium chromate; current = 0.5 amp; D anode = D cathode = 125; t = 20°

No.	Seconds	Voltameter Gas	Cell Gas	Cell Oxygen	Cell Hydrogen	Percent. Reduction	Mgms. Cr.
1	840	91.8	81.4	30.0	51.4	16.0	5.2
2	900	97.4	90.0	31.3	58.7	9.4	2.6
	5,400	....	....	....	....	....	...
3	1,000	99.8	96.3	32.7	63.6	4.3	2.0
	7,200	....	....	....	....	....	...
4	960	97.5	95.7	31.7	64.0	0.4	0.6

The extent of the reduction and the amount of metal deposition is less than was observed in the cases where other substances were added.

Nitric acid has also been added to the 14.28 per cent. chromic acid to form a solution holding 0.5 per cent. nitric. The results are given in Table XI.

TABLE XI.

14.28% chromic + 0.5% nitric; current = 0.5 amp;
D anode = D cathode = 125; t = 20°

No,	Seconds	Voltameter Gas	Cell Gas	Cell Oxygen	Cell Hydrogen	Percent. Reduction	Mgms. Cr.
1	990	94.0	76.0	31.2	44.8	28.4	6.8
2	960	92.4	80.4	30.6	49.8	19.1	5.1
	3,600	....	....	....	....	....	...
3	990	95.1	93.6	30.9	62.7	1.1	0.8
	5,400	....	....	....	....	....	...
4	960	94.2	93.8	31.1	62.7	0.16	0.4

The metal was dark colored, but nevertheless fair yields were obtained.

One run was made with hydrochloric acid as an impurity, its concentration being 1 per cent. The oxygen and chlorine in this as also in Table XIII were not determined separately.

TABLE XII.

14.28% chromic + 1% hydrochloric; current = 0.5 amp;
D anode = D cathode = 125; t = 20°

No.	Seconds	Voltameter Gas	Cell Gas	Cell Oxygen and Chlorine	Cell Hydrogen	Percent. Reduction	Mgms. Cr.
1	960	93.6	58.7	21.6	37.2	40.3	15.2

There is again to be noted high reduction, high oxidation and fairly good metal deposition.

With potassium chloride the results of the first run resemble in a very marked degree those obtained with hydrochloric acid. As in Table X, however, when the run is continued, oxidation, reduction and metal deposition soon cease.

TABLE XIII.

14.28% chromic + 1% potassium chloride; current = 0.5 amp; D anode = D cathode = 125; t = 20°

No.	Seconds	Voltameter Gas	Cell Gas	Cell Oxygen and Chlorine	Cell Hydrogen	Percent. Reduction	Mgms. Cr.
1	1,020	96.2	62.4	23.8	39.6	38.2	14.8
	14,400	.....	.....	.....	.....	.....	.....
2	1,020	95.0	95.0	31.5	63.5	.....	0.2

(h) Comparison of Efficiencies.—From the work of Geuther we may not tell exactly what current densities were used; but with an acid of the same concentration (14.28 per cent.) we have by adding impurities been able to obtain results which practically agree with his so far as the rate of metal deposition and hydrogen deficiency are concerned. This is readily seen by comparing 6 and 7 of Table I with 1 and 2 of Tables VIII and IX. Under no circumstances have we, by working within a temperature range of 20° to 90°, current density of 10 to 250 amperes, concentration from 1 per cent. to 50 per cent., been able with a *pure* acid to get results at all comparable with those of Geuther.

An attempt was made to duplicate Buff's experiment 4, Table III. With the 5.13 per cent. solution he had used electrodes 1.5 square inches in area; the current at its maximum had evolved in the voltameter 14.5 cc. of hydrogen per minute. This corresponds to a density of about 10 amperes per square decimeter, if both sides of the cathode are considered. With a voltage of 2.45, and current of 0.025 amperes, we made a run of 4,200 seconds; there was no metal deposition and no measurable reduction. The current was now increased to 0.08 amperes; the corresponding voltage was 2.66. Results are given in Table XIV.

TABLE XIV.

5.13% acid; current = 0.08 amp; D anode = D cathode = 20. Voltage = 2.66; t = 20°

No.	Seconds	Voltameter Gas	Cell Gas	Cell Oxygen	Cell Hydrogen	Percent. Reduction
1	4,020	64.5	63.2	20.1	42.3	1.6
2	3,720	60.4	60.0	19.9	40.1	0.5

For this run also no metal was found. The results correspond with those already found (page 126), and indicate that at the current density employed the decomposition voltage for metal deposition had not been reached.

It will be seen that the reduction, instead of being 95.7 per cent. as with Buff, is more nearly 1 per cent. While it must be admitted that the use of the same concentration, temperature and current density does not mean that the experimental conditions have been accurately reproduced, it would appear that the most reasonable explanation we can offer for the reduction observed by Buff and Geuther is that the acids they used were impure. Buff's results are not comparable with those of Geuther, since the latter was working above the decomposition voltage, while the former was using densities corresponding to voltages below this.

Our results prove conclusively that Placet and Bonnet were right in stating that metallic chromium could be obtained by the electrolysis of commercial chromic acid. We have made a large number of runs to find the effect of certain variables on the nature of the deposit. Platings made without stirring the solution and without finishing by buffing, etc., resemble the very finest work done with silver. In fact, for plating purposes the metal should have a great future before it. The average metal deposition in all our runs is somewhat over 0.1 gram per ampere hour.

The failure of so many chemists is probably due to the use of too low current densities, combined possibly with the belief that the electrodeposition from solutions of the acid was not possible.

The results of Reese were readily reproduced by using a current density which corresponded to a voltage lower than the decomposition voltage; with greater current densities, however, the purest acid is quickly reduced.

Greater efficiency of reduction and metal deposition has been obtained by the addition of sulphuric than with hydrochloric or nitric acid. The pure acid shows very low efficiency of deposition. It is our belief that while a purer acid might show still less, the actual deposition is not caused by the presence of impurity.

Why does the sulphuric acid increase the efficiency? It is well recognized by electrochemists that the efficiency of a metal deposition varies very considerably with the number of ions of the

metal present in the solution. With a small number low efficiencies are expected; as this number increases the efficiency will increase. We suggest, therefore, that the sulphuric acid has increased the number of chromium cations in the solution. It is probable that in its presence the dissociation of the chromic acid is forced back to the CrO_3 stage and that the secondary dissociation of this into hexavalent chromium cations is thereby increased.

Another method of expressing the same result is this: When sulphuric acid reacts with CrO_3, the latter behaves as a base and hexavalent chromium tends to be formed, although normally the trivalent salt is the more stable form. It does not seem at all improbable, therefore, that the various acids and also various salts tend to increase the ionization of chromium acid to hexavalent ions, and that this result is shown in the increase of efficiency of deposition of the metal.

(i) Products of Reduction.—In every case examined where the chromic acid was reduced, the solution was colored brown and the reactions showed the presence of chromic salts. When alkali was also formed at the cathode there was formed a brown precipitate, which on treatment with hydrochloric acid evolved chlorine. This is probably the compound already found by Geuther, Buff and Morges, who regard it as CrO_2 or chromium chromate.

A compound corresponding to the same formula has been made by other methods. For example, Maus[24] found that chromic sulphate or chloride treated with potassium chromate, or chromic hydroxide in the presence of chromic acid, reacted to form it. In other words, an oxidizing acid or the salt of the acid might be reduced by a compound in which the element occurred in a lower valency, to a product in which the element had an intermediate valency.

Now, these chemical conditions are the ones which have been reproduced in the electrolytic cell. In the solutions, to which were added sulphuric, nitric or hydrochloric acid, if a partial reduction could have taken place with formation of the chromic sulphate, nitrate or chloride, there would have been a reaction between these compounds and the chromic acid, with formation of the chromium chromate, heat also being evolved. In other

[24] Pogg, Ann. 9, 127 (1827).

words, the reduction to the CrO_2 stage would be more readily effected than the reduction to the trivalent stage.

So also, when an alkali salt was added, there might be assumed a tendency for the chromic acid to reduce at the cathode to the chromic salt, which either as chromic hydroxide or the alkali chromite would, according to the Maus reaction, tend to form CrO_2. In place of the reaction proceeding in two distinct stages, however, the one observed in the electrolysis was the precipitation of the solid. This was noticed with the solutions used in Tables X and XIII.

We have already noted that in every case examined the yield of chromium and the extent of reduction decrease as the reaction proceeds—that is, as the chromic acid changes to its lower stages of oxidation. The conclusion might at once be drawn that the presence of the reaction products decreased the efficiency, were it not that not merely is metallic chromium removed, but that the chromium chromate precipitates.

A solution was therefore selected in which this precipitation might to a certain extent be avoided—that used in Table VIII. With 2 cc. of this solution corresponding to 148 mgms. of the metal, five runs were made under the following conditions: Time, 960 seconds; current, 0.5 amp.; D anode = D cathode = 125, t = 20°. The weights of the deposit were 20, 18, 16, 15 and 4 milligrams respectively, while a slight amount scaled off. The total amount of chromium left in the solution was then about one-half the amount originally present. The sixth run was then made—this is number 6 in Table XV. The original solution was then diluted to one-half and a run made—1 in Table XV.

TABLE XV.

Chromic + sulphuric; Cr content = 74 mgms; current = 0.5 amp; D anode = D cathode; t = 20°

No.	Seconds	Voltameter Gas	Cell Gas	Cell Oxygen	Cell Hydrogen	Percent. Reduction	Mgms. Cr.
	700	75.0	65.7	23.7	42.0	3.8	1.0
1	660	70.5	40.0	21.9	18.1	61.0	15.6

While the conditions are not absolutely comparable, the different results obtained in 6 and 1 indicate that the presence of the chromium chromate causes a very decided decrease in the yield.

As stated above, the oxidation power of chromic acid is increased by the presence of an acid—in other words, the chromic acid is more readily reduced in the presence of an acid. Is it then possible to reduce the chromic acid quantitatively to a chromic salt by the agency of the current? Le Blanc[25] says it cannot be done unless a diaphragm is used. "Nur solange man, wie Street, in alkalischer Lösung arbeitet und das Chromoxyd sich unlöslich ausscheidet, wird die Regeneration zu Chromat an der Anode praktisch zu vernachlässigen sein, falls man nicht etwa Diaphragmen zu Hilfe nimmt." Buff[26] found that at low current density chromic acid acidified with sulphuric is readily reduced to chromic sulphate, and potassium chromate to chrome alum. To check his statement, we took 2 cc. of a 14.28 per cent. chromic acid, 2 cc. of concentrated sulphuric acid and 2 cc. of water. No diaphragm was used. With anode density of 750 amperes, cathode density of 50 amperes, a current of 3 amperes in 10 minutes effected complete reduction. Ozone formation was noted. This is a very easy method of reducing chromic acid when it is desired to avoid the introduction of organic impurities. The Grove cell offers an illustration of the case where the reduction effect is found when current is being withdrawn from the cell.

A cell which would offer considerable interest is composed of chromium and graphite electrodes in sulphuric and chromic acid. If a diaphragm were used, this would form a storage cell, but its efficiency would probably be very low.

The experiments recorded in Tables IV to XIII have shown, therefore, some of the conditions by which it is possible to pass from hexavalent chromium to what is probably the tetravalent chromium chromate stage, the metal being deposited while the electrolytic reduction proceeded, but not, however, until a definite voltage (current density) was reached. The experiment cited in the last paragraph has shown some of the conditions by which the hexavalent may be carried to the trivalent stage. Carveth

[25] Darstellung des Chroms, p. 72.
[26] Liebig's Ann. *101*, 8 (1857).

and Mott examined but a few of the conditions involved in the reduction from the chromic to the chromous salts, being concerned more with the efficiencies of metal deposition.

Commercial Methods.—It is now easy to see some of the difficulties which are involved in the continuous deposition of chromium from its solutions. If an anode were employed which was practically a pure chromium, in an electrolyte of chromic chloride or sulphate, it might seem difficult to select the conditions of concentration, temperature and current densities at which the rate of solution (apparent anode valency) was exactly counterbalanced by the rate of deposition of the metal. The solution must not become acid because of the ease of decomposition of the chromous salt; in fact, a slight alkali reaction seems to favor an increased cathode efficiency. It is very probable that the exact conditions for this deposition will be worked out and that, as in other cases, the sulphate (or chloride) will be the salt employed.

The use of chromic acid or chromates in acid solution will probably be restricted to the cases where fine platings are required, since the current efficiency is very low. The electrodeposition from a fused bath offers very distinct possibilities.

There is no doubt that as soon as the commercial demands warrant, methods for the electrodeposition of chromium in every form will be devised.

(j) Conclusions.—In the study of the cathode reactions, at least three, but more probably four or more, different stages of oxidation are met. This means that in the various solutions there are chromium ions with four different valencies. When the equilibrium relations between metallic chromium and its ions have been determined, the question will be decided as to whether or not the anode reaction is the converse of the latter.

In regard to the constitution of chromic acid solutions the following facts must be noted: (a) The study of the equilibrium relations point to the existence of free CrO_3—a radical composed of a conductor and a non-conductor of electricity. So far as we are aware, no known compound of such a combination is known which, conducting the current in aqueous solution, is not by the supporters of the theory of electrolytic dissociation supposed to be dissociated into ions. (b) Chromium as anode may dissolve to form CrO_3. If dissolving to form an ion this will be hexavalent.

There is a continuous passage from the conditions where it dissolves divalent (and everyone concedes its ionization, because a *salt* is formed) to the conditions where it dissolves hexavalent (where ionization has not been conceded, because an *acid* was formed). (c) Chromium may be deposited from chromic acid after a definite decomposition voltage has been reached.

1. This evidence, therefore, makes it seem very probable that in chromic acid there exists a number of hexavalent chromium cations in equilibrium with many other ions, and that chromium in chromic acid may be considered a reversible electrode.

2. The main part of the work of Geuther is correct. Metallic chromium is deposited in the electrolysis of solutions of chromic acid, but this requires a high current density, which in this case is synonymous with a high decomposition voltage. For example, using platinum wires as electrodes, Geuther used currents of from 0.07 to 0.35 amperes—very great densities, probably higher than we have used. On comparing with our own results the very great percentage reductions and the high metal depositions which he obtained, we conclude that his acid must have been impure. The oxygen excess which he found at the anode we have never been able to find; his admission that his tangent galvanometer was wrong probably explains this. After the decomposition point is reached, the efficiency of metal deposition and the reduction of the acid go hand in hand; a chromium chromate is probably formed.

The results of Buff are readily understood when the current density he employed is calculated. Under no conditions have we been able to get deposition of the metal at a current density as low as he used; nor have we with any but very impure acids been able to duplicate his results.

Like Buff, the other workers, Schick, Cowper-Coles and Ferée, have probably used too low current densities; it seems very improbable that their materials were purer than those used in the investigation.

Some of the claims of Placet and Bonnet are sound. It is very probable that solutions of commercial chromic acid and of chromates to which have been added various substances which aid in the reduction, may not be used in a continuous and economical process for the extraction of chromium, since the efficiency is so

rapidly decreased by the formation of the reduction products. By oxidizing these, however, it would be possible to continue the extraction of the metal, making the process continuous. There is nothing to prevent the use of this method in the laboratory for the purpose of making pure chromium.

By selection of the proper impurity (*e. g.*, sulphuric acid), we have been able in a continued electrolysis to recover in the metallic form more than half the total chromium present in the solution. Had the reduced products been oxidized, this yield could have been carried to any limits desired.

The criticisms of Le Blanc on the work of Geuther, Placet and Bonnet and Street need radical change. The only justification for such criticism was due to the experimental conditions not having been described in sufficient detail by the various workers.

3. Electrolytic chromium may occlude as much as 250 times its volume of hydrogen.

4. It is possible by the use of the current to reduce chromic acid to the trivalent chromic salts in the presence of an excess of a mineral acid.

As previously stated, we regard chromium merely as the type of a large number of elements which, according to the degree of oxidation, are either acid or basic in their properties. The methods which we have used should, we think, be capable of application to numerous other cases, such as the rare earth acids.

Of the work planned but a small part is completed. It is our hope that the interest attached to the work will induce other electrochemists to enter the field.

Cornell University.

DISCUSSION.

President Carhart: The paper of Dr. Carveth is open for discussion.

Dr. W. R. Whitney: I would like to ask if you cannot tell us something about the properties of this chromium as compared with that produced by the Goldschmidt or alumino-thermic

process. For example, is the ductility and hardness about the same as that of other chromium? Professor Burgess told us that electrolytic deposited iron was very brittle because of the hydrogen it contained. I was wondering whether the case was paralleled with chromium.

Dr. Carveth: One of the features which we early noticed was that the metal occluded a great deal of hydrogen. This accounts for the peeling which is noticeable in the silver-white deposit on this piece of metal.

The metal dissolves in hydrochloric acid without showing the periodic wave motion which Ostwald was able to show in his chemograph. A very pretty experiment which one can perform with this pure electrolytic chromium is this: Dissolve it in hydrochloric acid; it forms the chromous chloride. Drop into the chromous chloride solution a piece of platinum—the chromous chloride immediately evolves hydrogen at the surface of the platinum.

Here is a sample of so-called "pure chromium" purchased from an American maker. It analyzes about 99.25 per cent. chromium, with some aluminum, iron and silicon. This metal does not show the periodicities of solution which Ostwald had noticed with the Goldschmidt chromium. There is no doubt that the occurrence of periodicities of solution is due to the presence in the metal of impurities—probably iron and aluminum. We have not attempted to duplicate Ostwald's experiments by adding the various impurities, such as iron; but we hope that some one else may try to do this.

The tests of the physical properties we have made have not been very extensive. They have been confined mainly to qualitative tests as to the hardness. A sheet of copper like this may be readily cut with a pair of scissors, but when plated with a very thin layer of chromium it is extremelly difficult to cut. There is very little hydrogen occluded in this particular case. We have not carried out any experiments to test this point.

This specimen shows how an article plated with chromium can be twisted, and yet the deposit is not hurt. I think that shows that for plating work chromium has a future as soon as we find out the conditions of wear and tear which it can stand.

Mr. S. S. Sadtler: Can you use it as an anode and keep the bath in the same condition?

Dr. Carveth: We have not as yet succeeded in doing that. The anodic solution of the metal, unfortunately, is a very difficult one to control. From reading the work of Hittorf one might assume that the metal dissolves at the anode to form chromous chloride only. We have not found it so, but we have found that various oxy-chlorides are formed.

Dr. J. W. Richards: I should have preferred to see Professor Carveth use the term coulometer instead of voltmeter. I was misled in two or three places in seeing the term "volt," and thinking it expressed voltages, but found it to mean the readings of the coulomb-meter. I think it is a reform badly needed in electrochemical work. The deposition of chromium from these solutions, in which it may occur in so many different phases, as different salts of chromium and as chromic acid, is, I think, one which explains the difficulty of depositing chromium from its solutions. The possibility of oxidation at the anode and reduction at the cathode—a solution at the cathode recomposing and the reverse at the anode—is so great that I think that explains very largely the difficulties of obtaining the deposition. I have not studied this paper carefully; but I did look through it to see if any deductions could be made as to the critical voltage or determination of the minimum voltage necessary to deposit the chromium, because there is a great gap in our knowledge of the thermochemistry of chromium compounds. Chromium is the only common metal I know of for which the chemist uses "X" and puts his results in the form of "X +" a certain number, the one basic number which we need (the heat of formation of any chromium salt that you like) not being known. If from these results the heat of formation of any one of the chromium salts can be approximately determined, we can calculate the whole thermochemistry of chromium, because the relations between the different chromium salts are very well known. Within the last year I have been consulted by people who wanted to know what the thermochemistry of the chromium compounds were, working with sulphuric and chromic acid mixtures—that is, wanted to know what the thermochemistry of the possible reactions are. We have not the basis for that very interesting theoretical calculation. If this can be determined from any of the data which Mr. Carveth has obtained, I think it would be a considerable contribution to the theory of chromium salts.

A paper read at the Seventh General Meeting of the American Electrochemical Society, held at Cambridge, Mass., April 26, 1905. President Carhart in the chair.

THE ELECTROLYTIC PRECIPITATION OF SILVER.

By Ralph C. Snowdon.

The precipitation of metals by electricity has, until very recent years, been regarded as something more or less in the hands of an invisible and uncontrollable power, and if good or bad results were obtained in specific cases, the greater portion of the conditions governing them were attributed to luck. It has been the object of about a year's work in this laboratory to show that the precipitation of metals from aqueous solutions, particularly for plating purposes, is as easily controlled and as purely chemical as any of our processes, the electric current being simply a means to an end and having the nature of any of our power factors.

Considerable work has been done on the precipitation of the metals, zinc, copper and tin, to furnish a part of the experimental data in a report by Professor Bancroft before the International Electrical Congress at St. Louis,[1] on "Chemistry of Electroplating," and we have followed out the same lines in the subsequent work on silver.

It is a well known and accepted fact in general chemical practice that substances which are precipitated from solutions separate out larger crystals if they are precipitated slowly, and that an approximate relation exists between the size of the crystals and the speed of precipitation. The ordinary formation of barium sulphate from soluble barium salt solutions and of crystals of copper sulphate of extraordinary size from copper sulphate solutions may be cited as examples of this fact. Now the current controls the speed of the reaction in the case of electrolytic precipitation, so we are justified in saying that the size of the crystals of the metal decreases with the increase in current density at the cathode unless secondary or extraordinary reactions take place. Also the decrease in the size of the crystals due to the addition

[1] Jour. Phys. Chem., 9, 277 (1905).

of various organic and inorganic compounds to the electrolyte is to be expected from our present conception. Zinc, copper and tin all fall in line with the theory, and they also show a marked increase in size of crystal between 20 and 70 degrees, those at 70 degrees, all other conditions the same, being the largest. Rotating the cathode or stirring vigorously by other means tends to flatten out the crystals probably by simple skin friction, and it is possible to obtain a bright polished deposit in many cases by running up the speed of the cathode and using a correspondingly high current density. This apparent limiting speed and current density in the case of decreasing crystal size is of some interest in the precipitation of silver from solutions which usually do not give a satisfactory plating deposit. It is true that even our voltameter deposits are sometimes unsatisfactory because of their tendency to form large crystals and fall off.

Therefore the object in this investigation was to proceed with the study of the effect of current density and speed of rotation of the cathode upon the electrodeposition of silver, and to ascertain the possibility of obtaining a plating deposit of silver from the nitrate solution.

The first experiments were tried with a normal silver nitrate solution, silver anode and small rotating disc of copper plated with silver for cathode. This method of operation was of no use whatever because the reactions at the anode and cathode acted together in a manner detrimental to the purpose of the investigation, giving results seemingly independent of current density and speed of rotation. After several unsatisfactory runs this method of procedure was abandoned in the light of some recent work on the silver voltameter by Richards[1] and others, where they use a porous diaphragm to separate the anode and cathode solutions. By means of the diaphragm the peroxynitrate of silver, $3Ag_2O\text{-}5O\text{-}AgNO_3$,[2] which is formed at the anode is kept from the cathode and its influence is thus eliminated. Our cell was then changed to suit the new conditions by the addition of a 100 cc. porous cup which contained the silver nitrate solution under examination, and in which the cathode rotated. Outside

[1] Richards, Collins and Heimrod. Proc. Am. Acad., *35*, 123 (1899); Richards and Heimrod. Ibid, *37*, 415 (1902); Guthe. Phys. Rev., *19*, 138 (1904).

[2] Mulder and Heringa. Recueil Trav. Pays-Bas., *15*, 1 (1896).

the diaphragm and near its bottom was the platinum anode in its 20 per cent. nitric acid electrolyte. All was contained in a 500 cc. beaker. The cathodes were small copper discs, 7 cm.^{2} in area, soldered to a vertical shaft and speeded to about 2,200 R.P.M. by a small electric motor.. The lower face of the disc was plated with silver from a cyanide solution (to be described later) and then burnished. This operation was repeated two or three times in order to insure a non-porous deposit. The remainder of the disc stem and drop of solder were coated with paraffin, and we had by this means an inexpensive and efficient cathode. These cathodes were then rotated within the porous cup, a fresh one being used for each change in conditions. After each of the longer runs and each two of the shorter ones, we changed the silver nitrate solution which by continued use became more or less dilute and affected by diffusion of nitrate acid from the anode compartment.

Endosmose was also prevented by keeping the level of the cathode solution higher than that in the anode compartment and by previously saturating the porous cup with the silver nitrate solution. The diaphragm worked very successfully in keeping the anode formation from the cathode chamber and very excellent results were thereby obtained, which followed the line of prediction very closely.

The solutions of silver nitrate used were made up as follows:

1. Normal $AgNO_3$.
2. Normal $AgNO_3$, normal HNO_3.
3. 1/10 normal $AgNO_3$, 1/10 normal HNO_3.

Five runs on each of the solutions were made, using the following current densities, actual currents, voltages and times of run:

SOLUTION No. 1, T = 19°.

	Current Density Amp/dm^2	Actual Current Amperes	Volts	Time Minutes
1	0.5	0.035	1.20	30
2	2.0	0.140	1.33	10
3	4.0	0.280	1.62	10
4	10.0	0.70	2.55	8
5	20.0	1.40	5.60	5

SOLUTION NO. 2.

1	0.5	0.035	1.21	30
2	2.0	0.140	1.30	15
3	4.0	0.280	1.60	15
4	10.0	0.70	2.0	15
5	20.0	1.40	2.45	10

SOLUTION NO. 3.

1	0.5	0.035	1.25	30
2	2.0	0.140	1.80	15
3	4.0	0.280	.....	...
4	10.0	0.70	.....	...
5	20.0	1.40	7.4	10

We made photomicrographs (enlargement, 91 diameters) of each cathode as soon as it was dry, and then lacquered it to check tarnishing as much as possible. These photomicrographs show that the size of crystal decreases with the increase in current density, although the real difference between the size of the *crystal faces* in the first two runs of each set is very small and at times seemingly negative, but the *crystal aggregations* change regularly in size. The decrease in size of crystals between the third and fifth runs is genuine, although the change is not great, and it seems as though the maximum speed attainable with our motors is not suitable for the higher current densities. It is also noticed that the crystals in the cases of high-current densities are laid on in moundlike masses, following the direction of rotation, and are not separate individuals.

Therefore from these experiments we are justified in saying that, in the case of silver nitrate solutions, the size of the crystals of electrolytically precipitated silver increases with the increase in current density and that the "chemistry" idea is based on firm foundations. Some people have observed that rapid stirring of the electrolyte and a high-current density at the cathode tend to make a metal deposit smoother and more homogeneous. The

Elmore process for making seamless copper tubes is an instance of this. All other experimenters along this line have varied both conditions simultaneously, and, since this explained but little, the present work was carried out, varying only one condition at a time.

In the previous work on the silver nitrate solutions, we kept the speed of the cathode very nearly the same in all cases, so the actual effect of stirring could not be observed excepting in a general way. If this betterment of deposit in the case of rapidly rotated electrodes or unusually agitated solutions is due to simple friction of the electrode against the solution or the rapid renewal of discharging ions, then we should expect that a decrease in the rate of stirring would allow the deposit to become homogeneous, more crystalline or "treelike" and ultimately bad. In order to observe the effect of such a decrease in the rate of stirring, the silver cyanide solution again came into play because it gave the nearest to a bright deposit of any of the plating solutions. The solution is

15 g. $AgNO_3$.
Enough KCN to redissolve the precipitate formed.
1,000 cc. water.

Under ordinary conditions in a simple electrolytic cell with silver anode, this solution precipitates the silver as a beautifully white coating, having a matte appearance, but if the cathode be speeded to about 2,200 R.P.M. the deposit comes out almost bright. The conditions and results of experiments follow:

POTASSIUM SILVER CYANIDE SOLUTION, T = 20°.

1.	2.0 amp/dm²	Speed, 2,200 R.P.M.
	2½ minutes	Deposit, *nearly* bright.
2.	2.0 amp/dm²	Speed, 500 R.P.M.
	2½ minutes	Deposit, decidedly matte.
3.	1.0 amp/dm²	Speed, 2,200 R.P.M.
	5 minutes	Deposit, decidedly matte.
4.	10.0 amp/dm²	Speed, 2,200 R.P.M.
	5 minutes	Deposit, decidedly matte.

The copper cathodes previously described were used, but they were not plated with silver before the runs. A silver anode was

used. Several trials were necessary before the conditions were obtained for a bright deposit, working from a low-current density and a high-current density toward a happy medium. The data for these have been omitted because they indicate but little. The reason why the current density of 10 amp/dm^2 did not give a bright deposit is because the speed and current density are factors depending upon each other, and in this case the silver was precipitated out of the solution too rapidly to be burnished by the swiftly moving cathode. However, the difference between Run 1 and Run 2 shows that the ideas advanced are correct as far as we have gone and that the speed is a very important factor. The difference between 1 and 3 confirms still further the conceptions in regard to increase in crystal size with decrease in current density.

There is but little doubt that if means were at hand by which the cathode could be rotated at higher speeds a place would appear where a burnished deposit might be obtained from even a silver nitrate solution, one of the poorest solutions from which to precipitate a good deposit of silver.

During the investigation, the effect of glue on the deposition of silver was studied since it is usually conceded that the addition of organic "colloids" causes wonderful effects when precipitating metals chemically or by electricity. Three experiments, which were made on silver nitrate solution No. 1, gave rather interesting results. These were done in the diaphragm cell previously described. The lowest current density was used because it usually forms large crystals of the metal. Our conditions were as follows:

MOLECULAR SILVER NITRATE SOLUTION, No. 1, T = 19°.
Speed rotation, 2,200 R.P.M.

1.	0.5 g. glue per liter.	C. D. 0.5 amp/dm^2. Smooth purple deposit.
2.	3.0 g. glue per liter.	C. D. 0.5 amp/dm^2. Smooth yellow deposit going purple.
3.	10.0 g. glue per liter.	C. D. 0.5 amp/dm^2. Smooth purple deposit.

A precipitate of colloidal silver was obtained in each of the cases, Nos. 1 and 3 being purple in color and almost perfectly

amorphous, while No. 2 had a yellowish color which darkened slowly on standing to nearly purple. The three colloidal deposits which we did obtain had no visible crystal structure and were nearly bright. They resembled those precipitated by M. Carey Lea from silver salts of organic acids by purely chemical means. The phenomenon is rather unusual, and we have not tried to work out the conditions under which the various forms of colloidal silver may be obtained, but leave this for a further research. The general results of this paper are:

A very finely crystalline deposit of silver can be obtained from a silver nitrate solution by rotating the cathode rapidly and keeping the anode and cathode solutions separated.

The size of the crystals decreases with the increase in current density and the increase in the rate of stirring at the cathode.

The addition of small amounts of organic "colloids" to the solution makes the deposit very amorphous and causes the precipitated metal to assume a colloidal state.

The presence of free nitric acid decreases the size of crystals but slightly.

This work was suggested by Prof. Bancroft and carried out under his direction.

Cornell University.

DISCUSSION.

PRESIDENT CARHART: The point seems to relate to the deposition of nitrate of silver. I should like to make a very brief remark in connection with this paper. You all know that in the use of the silver coulomb-meter (not ampère-meter) it has been found that a dense anodic solution is formed; and, by the way, I suspect that a good deal of chemical work should be done to find out what happens at the anode in electrolytic deposition and decomposition. Dr. Hulett tried the experiment of agitating the anode by rotating it to see what effect this would have on the amount of silver precipitated by an ampère, and he found that it increased the precipitation beyond the number which is commonly received as the electrochemical equivalent of silver. The thought was that the

stirring of the solution might prevent the formation of the anodic compound; but instead of doing that it only served to distribute this compound, and the precipitation on the cathode was greater than where the solution was kept quiet. So far as we now know the method adopted by Prof. T. W. Richards, of keeping the anodic solution away from the cathode by having the level higher in the porous cup containing the cathode, is the only way to get uniform results.

Mr. S. S. Sadtler: At St. Louis, when Dr. Guthe spoke about his work with the silver coulomb-meter, I suggested that silver nitrite be used instead of silver nitrate. He took very kindly to that suggestion, and I am very curious to know whether any different results will be obtained with solution of silver nitrite instead of silver nitrate.

Prof. T. W. Richards: It might be of interest to note that silver nitrite has been tried in the coulometer in the chemical laboratory of Harvard College. We tried it in connection with the other experiments. We found that the amount deposited was not very different from that with silver nitrate. It is difficult, of course, to get a sufficiently concentrated solution. The nitrite is more liable to cause accidental decomposition during the deposition of silver than the nitrate, and is therefore less satisfactory than the nitrate.*

Mr. Edward F. Kern: Mr. Chairman, I have here a strip of cathode silver which, no doubt, will be of interest. On examining it you will find that it is very hard, solid and decidedly smoother than silver formed in the ordinary electrolytes, excepting the cyanide. This strip of silver was formed in an electrolyte of silver methyl sulphate ($AgCH_3SO_4$) containing about 6 per cent. silver and 15 per cent. methyl sulphate (CH_3SO_4), using a current density of about 22 ampères per square foot and an electromotive force of 0.35 to 0.45 v. There was also present an organic reagent, which caused the deposit of silver to form hard, smooth, and also preventing treeing. The anode was a small bar of Doré bullion, produced from electrolytic copper slimes, and the cathode was a thin sheet of silver greased with meat suet, from which this deposit was stripped. A description of the process will be found on page 145 of the "Electrochemical and Metallurgical Industry" of April, 1905.

* Z. phys. Chem., *41*, 311.

It was found that a hard, smooth deposit of silver could be obtained in either an acid electrolyte or silver fluo-borate ($AgBF_4$) or silver methyl sulphate ($AgCH_3SO_4$), arabic or gelatine, in 12,000 to 15,000 parts of electrolyte. If a larger amount or a smaller amount of the reagent is present, the silver does not deposit hard and smooth. When the amount of reagent is increased to one part in 5,000 parts of electrolyte, the deposit begins to darken, and when the amount of reagent is further increased, the deposit forms dark and spongy, the colloidal deposit of which Mr. Snowdon speaks.

We have made a number of experiments trying the addition of various organic substances, and also mixtures of them, to silver methyl sulphate electrolyte, and have finally found a very cheap reagent, whose presence in the proportion of one part in 5,000 parts of electrolyte, and even in larger amounts, causes the formation of a beautiful, hard, smooth deposit of silver, resembling a good deposit of copper. The advantage of this reagent is that it does not require the great care to get the right proportion, as does gum arabic or gelatine. When present in very large amounts, it does not cause the formation of the colloidal precipitate, or spongy deposits.

I would like to mention, as it might be of interest to Dr. Bancroft, that at the Betts' laboratory we have also succeeded in obtaining smooth, hard deposits of bismuth methyl sulphate. It was not found necessary to add any organic agent. The better deposits, however, were formed by using the methyl sulphate electrolyte. Smooth, hard deposits of antimony are also readily obtained. The electrolyte in this case is antimony fluoride (SbF_3). Mr. Betts' patents on "The Electrolytic Deposition of Antimony" fully describe the process, also on page 145 of the "Electrochemical and Metallurgical Industry," April, 1905, will be found a description of the apparatus used.

A paper read at the Seventh General Meeting of the American Electrochemical Society, held at Cambridge, Mass., April 26, 1905. President Carhart in the chair.

SOME RESULTS OF EXPERIMENTS WITH THE ELECTRODEPOSITION OF METALS ON ALUMINUM.

By Alexander Lodyguine.

Some years ago—to be more accurate, at the beginning of 1900—when I was connected with the Parisian branch of the Electric Vehicle Co., of Hartford, Conn., the idea struck me that if I could make plates for storage batteries of a very great surface, with a very thin layer of active matter, I could obtain a storage battery that I would be able to charge in less than one hour, and whose capacity would be several times greater, for the same weight, than that of any of the existing batteries, provided that the support for the active matter were very light.

I could not use lead for the support of the active matter because of its weight. Only two materials possessed the qualities necessary for this purpose: carbon and aluminum.

Carbon plates will probably be used for this purpose when they will cost less and will be less brittle. For the present only aluminum plates are available, and these only if they can be made unattackable by the electrolyte. To make them so, I undertook to cover them with layers of such metals as can resist the chemical action of the electrolyte.

One way I have of accomplishing this successfully is to cover aluminum plates with other metals by electrodeposition. I have, besides, other means than electrodeposition to reach the same result, but it would be a digression to speak of these here.

My aim was to cover as thin plates as possible of aluminum, with layers of antimonious lead or with antimony; these layers to be as thin as compatible with the complete protection of the aluminum from the action of the electrolyte.

The very first experiments showed clearly that I must avoid the formation of any compound of aluminum on the surface of the plate, whether soluble or insoluble. The presence of the

slightest traces of alumina, chloride or sulphate of aluminum, aluminates or alums absolutely ruined the success of the experiment; these compounds, on a negative aluminum plate, were finally all decomposed into alumina, or oftener into hydroxide of aluminum.

I soon came to the conclusion that the principal cause for the failure in depositing metals on aluminum lies in the difficulty to keep the surface of the aluminum not only strictly metallic, but free even from some compounds of aluminum in contact with it, and that not even the most vigorous scrubbing, brushing and washing, in alkalies, acids and water, suffices for arriving at these results.

I discovered that any electrolyte that attacks the aluminum must, therefore, be discarded, however slight and slow the attack might be.

On this account I found many electrolytes to be useless that are described in different books, and even patented, as very excellent for the purpose.

Some of those electrolytes were good when the strength of the solution was reduced, and were useless when at the strength described.

After many experiments, I came to the conclusion that I could not find (I do not say it is impossible) a good solution from which lead, or antimonious lead, could be deposed on aluminum plate.

I did not try the deposition of antimony directly on aluminum. I think now that I ought to have tried it from the same electrolyte I used for the deposition of antimony on copper, only greatly diluted, but what I did was to try first to cover the aluminum with some other metal solution that would not attack the aluminum, and then to deposit the antimony, or antimonious lead, on the plate thus protected.

You can see the results of my experiments with copper and antimony on three plates I have here.

Plate No. 1 is the plate covered with copper. It is intended for the plates of a storage battery. You can see that in some places the deposit is not so good as in others. It is entirely a result of a slight formation of some aluminum compound occurring even after the plate had been scrubbed, dried and brushed

in a weak solution of hydrochloric acid, brushed in running water, brushed in a weak solution of caustic soda, again brushed in running water, and was only after that put into the electrolyte.

Plate No. 2 was covered with copper after the same preliminary treatment; but the results, as you can see, are a great deal more satisfactory because the plate is smaller and it is easier to treat it more evenly.

No. 3 is a plate of aluminum, covered first with a coat of copper and then with a coat of antimony.

As can readily be seen, the coating of both metals stands bending and heating well. On one side of plate No. 2 you see some solder spread over a corner and adhering strongly enough for practical purposes; and the coat of copper on that plate is extremely thin. I believe that it is possible to cover aluminum with copper and tin it afterwards for many practical uses.

To deposit the copper on these plates, I used an anode of pure copper and an electrolyte of pure water with a few drops of sulphuric acid in it.

After the current had been passed through for some time, some sulphate of copper was formed, and from that sulphate of copper the copper was deposited, liberating the sulphuric acid, which formed more sulphate of copper.

The plate was taken out after half an hour and vigorously washed and brushed in water, in a solution of hydrochloric acid, in a solution of caustic soda and once more in water, after which it was again put into the electrolyte. The same operation was repeated several times, until the plate was evenly and entirely coated with a fine and adherent coat of copper.

After that the plate could be treated as an ordinary copper plate.

The electrolyte for the deposition of antimony on copper was suggested to me by the process of Mr. W. Borchers, described in the "Electrolytic Separation of Metals," by G. Gore, and by the process described by Mr. Edgar F. Smith, in his "Electrochemical Analysis"—article: Antimony.

My process, as also its results, is entirely different from both these, however, as in both cases the antimony obtained does not adhere to the cathode.

To deposit the antimony I used a concentrated solution of

protosulphide of sodium Na_2S, with the excess of the protosulphide in the vat.

Lumps of trisulphide of antimony, SbS, were placed into a porous cell of very oblong form, around a carbon plate. The cell was filled with the electrolyte and placed into a glass jar filled with the same electrolyte. Two plates of aluminum, coated with copper, were used as cathodes.

As can be seen, the antimony adheres firmly to the plate, is of very fine structure, and can be polished. The deposit can be continued as long as the monosulphide of sodium is not transformed into polysulphides. If I am not mistaken, this is the first time that antimony has been deposited continuously by electrical process, with decomposition of trisulphide, and in so fine a state.

I found that the best density of current for the deposition of copper on aluminum is about .0013 ampères per square inch, and that the same density of current gives excellent results for depositing antimony on copper.

The pressure of current I used for the deposition of copper on aluminum was about .5 volts, and for the deposition of antimony it was from 1 to 1.5 volts.

The amount of antimony deposited by one ampère in one hour was .833 grammes.

At that rate, from 1,080 to 1,620 KWH. are needed for the extraction of one short ton of pure antimony. At a price of current of $15 per KW. year, the cost of the above current for the extraction of one short ton of pure antimony is from $2.16 to $3.24.

The theoretical amount of antimony to be deposited in grammes per ampère hour, according to G. Gore, ought to be 1.4904 grammes.

A paper read at the Seventh General Meeting of the American Electrochemical Society, held at Cambridge, Mass., April 26, 1905. President Carhart in the chair.

SOME RESULTS OF EXPERIMENTS WITH THE REDUCTION OF TITANIFEROUS ORES.

By Alexander Lodyguine.

Titaniferous ores have always keenly interested me. I believe that in these ores lies the future of American industry, because on them depends the future of American iron and steel, and of many other industries besides.

Sooner or later, rather sooner than later, the magnetites, hematites, etc., now available for the large iron and steel plants will be things of the past, and these plants and others that will rise will have to cease operating or use other ores for the production of their iron and steel.

In this country there are, one may say, inexhaustible deposits of titaniferous ores. To be persuaded of the truth of this assertion one needs only to consult the list of deposits of these ores in different localities, and consider the amount of iron and titanium they contain.

The United States Geological Survey, with their accustomed kindness, furnished me a list of the more prominent localities in the United States where titaniferous ores are found, with the brief analyses of a number of representative ones, given below:

Table I.

	Iron Oxides	Titanic Oxides
Iron Mt., Col.	62.00	10.00
Iron Mt., Col.	70.50	14.00
Mayhew Lake, Minn.	80.78	12.09
Church Mine, Hunterdon Co., N. J.	69.40	10.52
Naughtright Mine, Morris Co., N. J.	89.39	7.50
Split Rock Mine, Essex Co., N. Y.	61.83	14.70
Iron Mt., Essex Co., N. Y.	55.82	16.37
Tunnel Hill, Essex Co., N. Y.	49.17	16.45
Little Pond, Essex Co., N. Y.	53.15	5.21
Lake Sandford, Essex Co., N. Y.	87.20	10.73
Lake Sandford, Essex Co., N. Y.	55.64	15.77
Rockingham Co., N. C.	66.56	13.71
Rockingham Co., N. C.	79.78	12.08

	Iron Oxides	Titanic Oxides
Cumberland Hill, R. I.	40.00	15.30
Cumberland Hill, R. I.	45.62	9.93
Cumberland Hill, R. I.	58.50	3.66
Near Laramie, Wyo.	61.99	23.49
Near Laramie, Wyo.	73.52	23.18
Near Laramie, Wyo.	73.01	22.43

The most important deposits of titaniferous magnetite, so far as size and accessibility are concerned, occur in the Adirondack Mountains, near Westport, Elizabethtown, and Lake Sandford, in Essex County, N. Y.

And yet the ironmasters of to-day will not allow over 1 per cent. of titanium in the ores they use, and many will not touch a titaniferous ore with tongs.

The difficulty is that these ores smelt hard in the now existing types of furnaces, besides choking the blast furnaces. New types of furnaces and new methods of smelting are needed for the purpose.

We all know that Mr. August J. Rossi, not *a* pioneer, but *the* pioneer, in this line, has consecrated a great deal of talent, labor, inventiveness and time in the development of this field, and has also accomplished a great deal; but the field is so large and has been so little tilled that there is still an abundance of room for many.

I have also tried my hand in this field.

For my experiments I had a titaniferous ore from Canada. The composition of that ore as given in a certificate of analysis from the Provincial Assay Office, Belleville, Ontario.

TABLE II

		Per Cent.
Total Metallic Iron	Fe	50.30
Silica	SiO_2	4.26
Sulphur	S	0.35
Phosphorus	P	0.06
Titanium dioxid	TiO_2	16.42
Manganese	Mn	0.18
Alumina	Al_2O_3	2.34
Lime	CaO	1.26
Magnesia	MgO	traces
Moisture		0.30

Titaniferous ore needs an electric furnace, and, as you will see, it can afford it.

My experiments were made with a little electric furnace of my own designing. The furnace capacity was two kilogrammes, or 4.4 pounds of the ore at a charge. The furnace could work continuously, but for the most part it was in operation only from time to time.

I am sorry that I cannot as yet give a description either of my methods or of the furnaces and other apparatuses I used, and intend to use, for the purpose. I am looking for an opportunity and the means that will enable me to realize my invention on an industrial scale and to cover it with patents. However, I can here give some results of my experiments with the reduction of these ores into steel and ferrotitanium.

From 2,000 grammes of ore I obtained, as an average, about 840 grammes of metal. The amount of iron in 2,000 grammes of ore being equal to 1,006 grammes, and the amount of titanium to 197 grammes, the loss in iron is equal to 16.5 per cent., and in metal to 30 per cent.

I give here the analyses of three different samples of iron, obtained from my furnace and by my methods from the same ore;

TABLE III

		Per Cent.		
		No. 1	No. 2	No. 3
Total metallic iron	Fe	97.57	84.70	80.34
Silicon	Si	.40	.40	1.40
Sulphur	S		.60	.20
Phosphorus	P		.08	.09
Titanium	Ti	traces	13.79	17.22
Aluminium	Al	traces		
Calcium	Ca	.33		
Carbon	C	some		
Total of chemically pure metal		97.57	98.49	97.56

The lot of ore of which sample No. 1 was produced was treated quite differently from the lots that produced samples No. 2 and No. 3, and the two latter differed slightly in treatment from each other. The treatment of the lot of ore for sample No. 1 was intended to produce iron free from any titanium, while with the lots of ore for Nos. 2 and 3 the intention was to retain as much titanium with the iron as possible.

As I said before, 16.5 per cent. of iron was lost in the smelting of the ore. The analysis of the slag left after smelting sample No. 1 gave the following results:

Fe—22.46%; SiO_2—14.77%; Al_2O_3—14.55%; CaO—8.27%; TiO_2—17.07%.

From this slag ferrotitanium, very rich in titanium, can profitably be extracted.

The amount of energy I used for my experiments was equal to 11,250 watts. The time needed to transform the ore into metal was about 8 minutes. This time could be divided into two periods, one, equal to about 5 minutes, was the time needed to raise the temperature of the furnace and the ore to the point where it was ready for reaction, and the other, equal to about 3 minutes, was the time taken by the process of reaction, *i. e.,* the reduction of the ore properly speaking. It is evident that if the furnace worked continuously the duration of the first period would be reduced. Taking the duration of the whole experiment, the amount of energy required for the reduction of 840 grammes of iron or ferrotitanium would be 11250X8 : 60 = 1.5 KWh., which means that for the reduction of one short ton of steel or of ferrotitanium, in my furnace and by my method, about 1,570 KWh. would be needed.

The approximate cost of one short ton of steel, reduced from titaniferous ore, calculated on the above given bases and produced in a reasonably large factory, would be something like what follows:

TABLE IV

Ore (magnetic, metallic iron 50.3 per cent) 2.100 tons at $1 per ton..	$2.100
NOTE.—Cost of mining from 25 to 50 cents a ton; loading and unloading and shipping of the same to the smelting furnace, 50 cents a ton. Total from 75 cents to $1.	
Flux, reducing agents and other materials	2.800
Electrodes	1.125
Electric energy	
$15 per KW. year { for smelting process—O. 180 KW. year	2.700
$15 per KW. year { for production of power, telpherage, cranes, traction, etc.—O. 195 KW. year	2.925
Labor { skilled	0.720
Labor { ordinary	1.050
Repairs, maintenance, etc	1.200
General expenses	0.900
Unexpected, underestimated, etc	0.270
Amortization	0.360
Total	$16.15
Returns from selling byproducts	7.50
The real cost of the manufactured steel	$8.65

In this high value of the byproducts lies the real advantage of titaniferous ores.

The byproducts that are obtainable from reduction of titaniferous ore into steel are many, and they are all valuable.

Ferro-titanium is one of them. When it contains a small amount of titanium, it is excellent for the wheels of railroad cars. It stands tear and wear a great deal better than any other steel. Evidently there exists a large market for such a product. When it contains more titanium it is so hard that it can be used for cutting glass, etc.

Titanium carbide is another valuable byproduct. This material is a great deal harder than carborundum, and can not only stand its ground in competition with it, but can even conquer a large market from its rival. It can be used in very large quantities in the metallurgy of iron and steel.

The *Mordants* and *pigments* of titanium are of great value and can also have a large market.

The *silicide,* the *boride* and the *nitride* of titanium are nearly as hard as diamond, and can polish and cut any precious stone, including the diamond.

On page 112 of the "Report of the commission appointed to investigate the different electro-thermic processes for the smelting of iron ores and the making of steel in operation in Europe," there is a table giving a comparative cost of the production of a ton of pig iron in an electric and in a blast furnace:

TABLE V

ELECTRIC SMELTING.		BLAST FURNACE.	
Ore	$2.76		$2.72
Coke 0.34 ton	2.38	0.925 tons	6.40
Electrodes	0.77		nil
Lime 400 lbs	0.40	400 lbs	0.40
Labor	0.94	American practice	0.42
Electric energy	3.50		nil
Steam raising for blow. engine	nil		0.10
Miscellaneous materials			
Repairs and maintenance, say	1.30		1.30
Total	$12.05		$11.34

The cost of the electric energy is assumed to be $10 EHP. year, or about $13.30 per KW. year; and the cost of the fuel for the blast furnace is taken to be $7 per ton.

But it would be unfair to compare the value of the metal obtained in my experiments with the value of the metal obtained in the experiments of the commission, or of the products of a blast furnace.

The average composition of the metal obtained by the commission from Mr. Keller's furnace is as follows:

TABLE VI

	Per Cent.
Iron	89.556
Carbon	4.200
Silicon	1.910
Manganese	4.300
Sulphur	0.007
Phosphorus	0.027
Total	100.000

The composition of the metal from the blast furnace varies in amount of pure iron from 84 per cent. to 94 per cent.

The transformation of such metals into steel, by electrical process, would cost about $4 more, and by Siemens process $5.50 more (page 73-74 of the report). The cost of Bessemer steel would be only about $3.50 more (page 114 of the report).

This brings the cost of metal similar to mine entirely produced in the electric furnace to $16.05; to $15.34 if the pig iron is made in the blast furnace and finished in the electric furnace; to $16.84 if the iron is made in the blast furnace and finished in Siemens' furnace; to $15.55 if the pig iron is made in the electric furnace and finished in the Bessemer converter; and to $14.84 if the pig iron is made in the blast furnace and finished in the Bessemer converter.

The value of the steel produced by these different processes will also be different. The steel of the highest value will be produced in the electric furnace entirely, and steel of the lowest value will be produced in the blast furnace and finished in the Bessemer converter.

It is evident that the average cost of production of steel similar to mine, in the electric furnace, as calculated by the commission, will be about the same, *i. e.*, $16.05, against mine of $16.15.

However, the cost of production of steel from the blast furnace and the Bessemer converter at a little lower price ($14.84 against $16.15, the difference being $1.31) is compensated for, not only by the higher grade of the metal of electric furnace, but beyond all comparison by the highly valuable byproducts which reduce the cost of the steel by nearly one-half, and which it is impossible to obtain by the old blast furnace method.

DISCUSSION.

PRESIDENT CARHART: Are there any remarks to be made upon these two papers?

DR. J. W. RICHARDS: The subject of the deposition of other metals upon aluminum is an important one, because there are some uses for which aluminum, because of its lightness, is very well suited, and yet for which, because of its attackability by acids (some of the ordinary acids) and alkalis, it is unsuited.

There is quite a large field in the commercial application of a satisfactory plating process by which some of the metals, such as nickel and chromium, can be plated upon aluminum so as to give it a surface resistance to corroding agencies. That would extend considerably the field of application of aluminum. The decomposition of chromium, for instance, metallicly upon aluminum has been commercially practiced in order to give to the surface of the aluminum a resistance which the chromium possesses and which the aluminum does not.

With regard to Mr. Lodyguine's other paper it would have been interesting to know under what conditions Mr. Lodyguine was able to make by reduction an iron containing only traces of titanium, while under other conditions, not stated, he obtains iron with 13 to 17 per cent. of titanium. This, I think, is the real test of the value of the process. If iron free from titanium can be regularly made economically from these titaniferous ores of Canada, there is a possibility that the electrolye-furnace method may be used on those very large deposits of titaniferous ores; but the conditions under which the iron can be reduced and the titanium not, with the production of a properly fusible slag, is, I think,

the point where any commercial importance of the process will have to show itself.

Mr. A. J. Rossi: I have made something like 50 tons of that pig iron electrically by adding to the ores enough carbon to reduce the oxide of iron and not the titanic acid, and, under a moderate current, it can be effected exactly as you get it in a blast furnace without practically any titanium, not more than two or three hundredths of 1 per cent. (0.02-0.03%), to possibly 0.05 per cent.

With proper currents I have also made alloys—ferro-titanium, containing 10 to 80 per cent. titanium (with or without carbon), by using either carbon or an aluminum bath as reducer. I have some specimens of such alloys, as also of curious electric furnace products. If the Society is interested to see them, I will be pleased to exhibit them, *as suggested by the Secretary.*

So far as concerns the extent of the deposits that Mr. Lodyguine spoke about, nobody can realize what they are without seeing them. Right in Essex County I have seen a deposit of iron 600 feet wide, and you can follow it for 2,000 feet, within a few feet from the surface. Millions of tons could be quarried in an open quarry. The ores contain from 57 to 60 per cent. of metallic iron, with some 15 per cent. titanic acid. In Canada some of these ores are also very abundant, containing from 25 to 50 per cent., and even 50 per cent. or more, of titanic acid.

A few years ago in Buffalo I treated some of these ores in a small blast furnace which was only 20 feet high by 4½ feet bosh, and we had a run of three or four months, without any trouble whatever, using all the ore I had on hand.

The method consisted merely in treating titanic acid as you would so much silica; that is, making a slag with the silica and titanic acid from the gangues of the ore on the one hand, and the added limestone and the ashes of the coke on the other. A titano silicate of the earthly bases was thus formed just as you would form, as slag, a silicate of these bases, with ores not containing titanic acid.

From this furnace we ran slags containing 37 per cent. titanic acid and 15 per cent. silica, which melted and ran perfectly well, and I had to assist me in this run a blast furnace manager from Catasauqua, Mr. John C. Hazard, who was present all the time, and had his helper and founder to take charge of the furnace. But

this had nothing to do with electrical smelting, though called for incidentally by Mr. Lodyguine's paper.

From my runs in pig iron electrically smelted I found that you want for about a gross ton (2,240 pounds) of pig iron a day something like 200 horse-power, possibly 185 to 190 may prove enough; I should say about 200 horse-power would be the proper power per ton day, practically, under ordinary circumstances.

You will find out the figures of cost very much like those of Mr. Lodyguine in *the conditions* he mentions. It may be said that in specially favorable conditions of localities, where the ore can be had cheaply, at the cost of mining so to speak, and where the electrical horse-power could be delivered or created at a low rate per year, electric smelting of pig iron could certainly compete favorably with the blast furnace for limited production.

However, with a production of 500 tons per day (not exceptional in the Pittsburgh district) would require 100,000 electric horse-power, and this power cannot certainly be found at 200 horse-power per ton except in a few localities, and surely not duplicated in the same. This brings forth a subject which I will treat before the Society in the next paper to be read to-day, viz: the utilization of the waste heat from the blast furnace gases. Were these gases to be used extensively in gas engines it would open up possibilities for electro-metallurgy in general to which I desire to call your attention.

As to the quality of the iron or steel obtained from those titaniferous ores electrically (or otherwise), it has been admitted, I think, by everybody that it is superior. The specimens of electrically smelted pig iron, of ordinary pig iron or steel treated with ferro-titanium alloys, that I will exhibit to you, and tests made of these products, prove this, and so far as one can judge of the quality of iron by its fracture, you will be able to ascertain this for yourself.

A paper read at the Seventh General Meeting of the American Electrochemical Society, held at Cambridge, Mass., April 26, 1905. President Carhart in the chair.

ON THE SPECIFIC INDUCTIVE CAPACITY OF OLEIC ACID AND ITS SALTS.

By Louis Kahlenberg.

In the course of some of his previous work the writer found that the oleates and also their solutions in various solvents are good insulators. It is the purpose of the present investigation to determine the dielectric constant of free oleic acid and of a number of its typical salts. The method of measurement employed was the improved form of Drude's method,[1] using the Tesla transformer. As it was not feasible to work with very large quantities of the substances tested, the apparatus employing the small condenser was used. The apparatus was carefully calibrated, using benzine, acetone and water, and mixtures of these liquids whose specific inductive capacity had been determined by Drude.

Three different samples of oleic acid were tested at 20° C. A sample of Kahlbaum's best oleic acid gave the result 2.50; a sample from Schuchardt had a D. C.[2] of 2.60; and another sample purchased from Bausch and Lomb yielded 2.57 as its D. C. These specimens were all quite fresh and clear in appearance. While at work on the oleic acid Dr. Herman Schlundt, of the University of Missouri, also determined the D. C. of this substance at my request. He informed me by letter that the sample he had in his laboratory possessed a D. C. of 2.28, stating, however, that the substance was rather dark in color and that no further purification was attempted.

Ferric oleate of Schuchardt's manufacture was found to have a D. C. of 2.68 at 20° C. Aluminum oleate from the same source had a D. C. of 2.40 at 20° C. Copper oleate prepared in this laboratory showed a D. C. of 2.80 at 20° C. in the solid state.

[1] Drude's Annalen *8*,336 (1902).
[2] The abbreviation D. C. stands for dielectric constant, or the synonymous term specific inductive capacity.

This substance was also measured in the liquid state at a temperature slightly above its melting point, but the result obtained did not vary from that just given beyond the limit of experimental error.

Sodium oleate, pure and anhydrous, prepared in this laboratory, was found to have a D. C. of 2.75 in the solid state at 20° C. When carefully heated to its melting point the result changed but slightly, the figure found being 2.83. Oleate of lead of Schuchardt's manufacture had a D. C. of 3.27 in the solid state at 18° C. At its melting point in the liquid form the value 3.70 was obtained.

A fine sample of cotton-seed oil had a D. C. of 2.30, while a sample of corn oil (made from Zea maize) showed a D. C. of 2.50. Both specimens were measured at 20° C.

Through the kindness of Dr. S. M. Babcock, of the Agricultural Experiment Station of the University of Wisconsin, eight samples of pure olive oil, made from California olives obtained from various localities of the latter state, were placed at my disposal. These eight samples were found to have the following dielectric constants at 20° C.: 2.60, 2.55, 2.70, 2.45, 2.60, 2.60, 2.53, 2.70.

In the course of the investigation the dielectric constants of four other oils were measured. The results obtained are mentioned in this connection merely to put them on record. The dielectric constants are as follows: Linseed oil, 3.25; rape seed oil, 2.35; palm oil, 2.40; colza oil, 2.70.

Most of the oils mentioned have also been measured by earlier investigators whose results, as a rule, run somewhat higher than those given above. This is particularly the case with the dielectric constants of olive oil and cotton-seed oil, as may be seen by referring to the excellent compilation of L. Graetz in Winkelmann's Handbuch der Physik 2 Aufl. Band 4.

From the data recorded above it appears that oleic acid has about the same dielectric constants as the oils which represent its esters with glycerine as the base. Moreover, the D. C. of oleic acid must be regarded as quite low considering that the compound is unsaturated and that it contains the carboxyl group. With the exception of aluminum oleate, the metallic oleates measured have a slightly higher D. C. than free oleic acid, the results obtained apparently indicating an increase of D. C. with increase of the chemical equivalent of the metal used. It is of special interest that

the specific inductive capacity of oleic acid is so slightly changed by the introduction of heavy metals into the compound. It would seem as though the characteristic electrical properties of the metals were almost entirely overcome by union with the large fatty radical of the oleic acid. It is further noteworthy that the oleates have nearly the same D. C. whether in the solid or liquid state.

Pyridine has a D. C. of 12.5. The D. C. of a saturated solution of copper oleate in this solvent was found to be 10.5, showing a diminution of the D. C., as one would naturally expect from the low D. C. of copper oleate. The specific inductive capacities of solutions of various oleates in a number of typical solvents are now being determined in this laboratory in order to ascertain the effects produced by the oleates in various cases. The complete results of this investigation will be published in the course of the year. It may be stated here, however, that as far as the work has gone the results indicate that the oleates diminish the dielectric constants when dissolved in solvents of high D. C., and increase the dielectric constants when dissolved in solvents of lower D. C. than that of the oleates employed, thus indicating that the results are such as would naturally be expected.

My thanks are due to Mr. J. H. Mathews, who has aided me greatly in making the above measurements.

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A paper read at the Seventh General Meeting of the American Electrochemical Society, held at Cambridge, Mass., April 26, 1905. President Carhart in the chair.

THE ROTATING DIAPHRAGM.

By Wilder D. Bancroft.

If we electrolyze an acidified copper sulphate solution between copper electrodes, noting the corresponding voltages and current, the resulting voltage-current curve will be very nearly a straight line passing through the origin. The pitch of the line gives an approximate measure of the specific resistance of the solution in the cell. If we interpose between the electrodes a non-conducting cylindrical diaphragm, which fills up most of the cross-section of the electrolytic cell, the resulting voltage-current curve will be very nearly a straight line passing through the origin as before, because no counter electromotive force has been introduced. The pitch of the line will be steeper because the resistance is greater. A glass or porcelain tube or rod will serve well as a diaphragm of this type. If we replace the glass tube by a copper tube or rod of the same size, we introduce practically no polarization, and the copper conducts better than an equal volume of solution. Our voltage-current curve, therefore, will be very nearly a straight line passing through the origin, but it will lie below both the other curves because the resistance in the cell has been decreased by the replacement of copper sulphate solution by metallic copper.

If we replace the glass tube by a cylindrical graphite rod of the same size, we bring about a new state of things. The graphite rod conducts much better than an equal volume of solution, but we now have the effect of polarization to consider. When the current flowing through the cell is small, the fall of potential per centimeter is also small. Under these circumstances practically no current will flow through the graphite diaphragm, and it will behave very nearly like the glass diaphragm. Owing to the possibility of a slight depolarizing effect around the dia-

phragm a little more current will flow for a given voltage with the graphite diaphragm than with the glass diaphragm. As the current through the cell is increased we soon reach a point at which copper is deposited on one side of the graphite rod while oxygen is set free on the other side. Since a portion of the current is now flowing through the diaphragm, the voltage must be lower than that required to give the corresponding amount of current in the cell with a glass diaphragm. With a still higher current flowing through the cell we reach the point at which the superior conductivity of the graphite diaphragm, as compared to an equal volume of solution, just compensates for the polarization. At this point the same voltage gives the same current both with a stationary graphite diaphragm and with no diaphragm. With still higher currents the voltage-current line becomes a straight line parallel to the line for a non-polarizable graphite diaphragm or a copper tube of the same resistance as the graphite rod, provided the polarization remains practically constant. There is nothing new about this, but it is unfortunately necessary to the theory of the rotating diaphragm.

If we take our stationary graphite diaphragm after copper has been deposited on one-half of it and reverse its position by rotating it through 180°, the precipitated copper will dissolve and copper will precipitate on the graphite surface facing the copper anode. Until the copper on the surface facing the copper cathode has been removed completely, the polarizations at the two faces will balance each other and we shall have temporarily a non-polarizable diaphragm. Instead of reversing the diaphragm every so often, we may rotate it rapidly. If we postulate 100 percent anodic and cathodic efficiency in acidified copper sulphate solution, any cathode polarization or precipitation of copper on one face of the graphite diaphragm will be removed at once as the diaphragm rotates, provided it rotates rapidly enough. Under these circumstances a rotating graphite diaphragm will behave like an ideally-reversible electrode. There will be no polarization and no precipitation of copper. The voltage-current curve will be very nearly a straight line passing through the origin and lying below the curve for no diaphragm, because the graphite conducts better than an equal volume of solution.

Mr. Snowdon was good enough to test these various predictions for me. A rectangular glass tank was filled with an acidified copper sulphate solution, $M/5CuSO_4 + M/5H_2SO_4$. Copper sheet electrodes, 50 cm^2, were placed 18.5 cm apart at the two ends of the tank. Near the middle of the tank a graphite rod 3.2 cm in diameter was pivoted so as to rotate round a vertical axis. The vertical length of the graphite rod in the solution was 7.5 cm. By means of a U-shaped wooden diaphragm cemented into place the cross-section of the tank at the point where the graphite rod was pivoted was cut down so as to be but little larger than the graphite diaphragm. Voltage-current determinations were then made with a stationary graphite diaphragm, with a rotating graphite diaphragm, with a glass cylinder substituted for the graphite rod, and with no diaphragm at all. The speed of rotation was about 200 revolutions per minute. The results are given in Table I.

TABLE I.

Current	Glass Tube	Stationary Graphite	Rotating Graphite	Without Diaphragm
Ampères	Volts	Volts	Volts	Volts
0.2	0.95	0.7	0.5	0.6
0.63	3.83	3.2	1.7	2.5
1.1	6.36	5.1	2.92	4.08
1.5	9.0	6.2	3.85	5.3
2.0	11.5	7.5	5.1	6.8
2.5	. . .	8.65	. . .	8.6*
3.0	. . .	9.75	. . .	10.2*
3.5	. . .	11.0	. . .	11.8*
4.0	. . .	12.1	. .	13.5*
4.5	. . .	13.2	. . .	. . .
4.76	. . .	13.75	. . .	. . .

* By extrapolation.

These data confirm the predictions. We get practically straight voltage-current lines with the glass diaphragm, with no diaphragm, and with a rotating graphite diaphragm. The voltages for the rotating diaphragm are lower than the corre-

sponding values with no diaphragm present. There is no visible precipitation of copper on the rotating diaphragm. The voltage-current curve for the stationary graphite diaphragm is not a straight line. At low currents the voltages approximate those for the glass diaphragm, though they are always lower. At about 2.5 amperes the curve cuts the extension of the line for the system without any diaphragm. Copper is precipitated on one-half the diaphragm, while oxygen is set free at the other half.

When the anodic and cathodic efficiencies are exactly 100 per cent., the rotating graphite diaphragm shows no polarization and behaves exactly like a reversible metal diaphragm having the same resistance. If the anode and cathode efficiencies are not 100 percent, this relation no longer holds, and the results will vary in each special case, depending on the relative efficiencies.

It may be of interest to consider the relation of the rotating diaphragm to the mercury diaphragm. In the Castner process we have a metallic diaphragm reversible with regard to sodium, and the sodium is carried from one mercury surface to the other, chiefly by a surface flow due to rocking. In the Rhodin cell the same result is obtained by centrifugal action. With a solid diaphragm there can be no diffusion and no surface flow, so the depolarization must be effected by rotation. The rotating diaphragm is therefore the analogue of the Rhodin mercury diaphragm, the difference between the two being the necessary result of one being solid and the other liquid.

In the experiments described we have eliminated polarization by means of rotation. It remains to be seen whether this process is reversible and whether polarization could be made to cause rotation. If the graphite diaphragm were suspended so as to rotate on a horizontal axis, copper would deposit on one side, making it heavier and causing it to revolve. An apparatus with a metal cylinder instead of a graphite one was patented by Sprague in 1881.[1] If we suspend a metal strip in a solution between a pair of metal electrodes, the voltage necessary to produce a given current will be a minimum when the interposed strip lies directly between the electrodes with its axis parallel to the lines of force. From the theorem of Le Chatelier we should expect the system to tend to adjust itself so that the electrical

[1] Cf. Wiedemann. Elektrizität, *2*, 505.

stress should be a minimum. Something of this sort appears to have been observed by Davy, who seems also to have been the first to observe some of the properties of what are now classed as perforated metallic diaphragms. Davy says[2]: "The manner in which aqueous fluids receive and communicate electrical polarity is shown by a very simple experiment. Let a number of fine metallic surfaces or flattened wires (of tin, for instance) be made to swim in a narrow trough containing water, and let two wires from the extremities of a voltaic battery of 1,000 double plates be plunged into the remote ends of the trough, one into one end, the other into the other end. The metals swimming on the water will immediately acquire electrical polarity; and the positive and negative poles will be regularly opposed to each other, the pole of the metal opposite to the wire positively electrified will be found to be negative, giving off hydrogen; the other pole will deposit oxide; the next wire to this will present the alternate order which will be preserved in all of them; those most remote from the right line of the circuit will be least affected. If the battery be in a highly active state, the different wires will attract each other by their opposite poles, and the circle will at length be closed with the production of brilliant sparks. The phenomena are precisely analogous to those phenomena in *magnetism,* presented by a number of flattened wires of soft iron, made to swim upon water, and rendered magnetic by the opposite poles of two powerful magnets; each wire has a north pole and a south pole, and in the alternation the different poles are attractive of each other."

I have tried a few experiments with copper wires and foil suspended in a copper sulphate solution between copper electrodes, using low voltages. Effects due to surface tension and to convection currents are so great under these circumstances as to mask the magnetic effect, which, however, must exist.

The general results of this paper are:—

1. A rotating graphite electrode in an acidified copper sulphate solution behaves like an ideally-reversible electrode.

2. No visible amount of copper precipitates on such a rotating electrode, though a considerable proportion of the total current flows through the electrode.

[2] Collected Works, *4*, 124.

3. The directional effect on a floating or suspended electrode of a small difference of potential is small and can easily be masked by surface tension phenomena and convection currents.

Cornell University.

DISCUSSION.

Mr. E. A. Sperry: While sitting here I have made a calculation as to the velocities—actual surface velocities—of the rotating diaphragm as it was called, and find them exceedingly small. It seems to me that there is an action that is possible to utilize in the arts; and I would like to make the suggestion that some of you who have students under you, as opportunity offers, and if it is possible, find the minimum of speed at which no deposition takes place under the conditions named. This can be very easily ascertained, and it may have a bearing on the rapidity of the surface action of the ions.

I might say that this surface rotation that Dr. Bancroft speaks of is only .074 mile per hour—an exceedingly low rate; and the question is, how much lower can it be made and still duplicate Dr. Bancroft's results.

President Carhart: It would be a little higher in centimeters per second, wouldn't it? (Laughter.)

A paper read at the Seventh General Meeting of the American Electrochemical Society, held at Cambridge, Mass., April 26, 1905. President Carhart in the chair.

ON THE HEAT OF SOLUTION OF ALUMINUM BROMIDE IN ETHYL BROMIDE.

By Harrison E. Patten.

INTRODUCTION.

The work presented in this paper was undertaken mainly to ascertain whether the heat of formation of anhydrous aluminum bromide, when added to the heat of solution of this salt in ethyl bromide, would permit of calculating the voltage required to deposit aluminum and bromine from this solution.

In a former paper[1] the conditions requisite for the deposition of metallic aluminum from a solution of aluminum bromide in ethyl bromide were stated. The decomposition voltage is there given as 2.3 volts, and compares well with the total potential difference (2.235 volts) between aluminum and platinum in a similar solution. The decomposition point of aluminum bromide in aqueous solution as calculated from thermal data is 2.997 volts. Anhydrous aluminum bromide is formed with a liberation of 119,700 small calories. Using this value[2] we get 1.748 volts theoretically required to decompose the dry salt. Its heat of solution in water is 85,300 small calories, which corresponds (by the same formula[2]) to 1.249 volts.

Now if we subtract 1.748 volts from 2.3 volts, the decomposition point in ethyl bromide solution, there remains 0.552 volt, which should represent the heat of solution of aluminum bromide in ethyl bromide. So it is desirable to know the heat evolved when aluminum dissolves in ethyl bromide.

Since the variation of molecular conductivity with the dilution is abnormal from the viewpoint of the theory of electrolytic disso-

[1] An Analytical Study on The Deposition of Aluminum from Ethyl Bromide Solution. Jour. Phys. Chem., *8*, 548, (1904.).

[2] $\frac{119{,}700 \times 4.24}{3 \times 96{,}540} = 1.748$ volts.

ciation, as shown by Plotnikoff,[3] the heat effect might afford an explanation of this irregularity. Further, Gustavson[4] states that $AlBr_3$ and C_2H_5Br react to give $AlBr_3C_4H_8$, but not until the temperature reaches 38°. However, when this $AlBr_3C_4H_8$ is once formed, it is said to react upon ethyl bromide at ordinary temperature, presumably to give $C_4H_7C_2H_5AlBr_3 + HBr$. It is a fact that sealed test tubes of ethyl bromide-aluminum bromide solution, after standing at room temperature for two months, exploded under the pressure generated. And in some experiments made to ascertain the conductivity of such a solution as it passed the critical point there was a regular increase in the electrical conductivity at 25° C., although the tube had been heated no higher. So in this connection, too, the heat of solution will have interest.

EXPERIMENTAL.

Weighed quantities of ethyl bromide contained in a stoppered glass flask were brought to nearly constant temperature in a nickel-plated copper calorimeter containing some 500 c. c. of water. The calorimeter was protected from radiation by a large glass beaker coated with tinfoil, and standing on cork in a Berthelot water jacket of suitable size. The aluminum bromide was broken from its glass test tube container into the ethyl bromide, and the percentage composition of the resulting solution calculated from the gain in weight—since in every case the salt dissolved completely.

The rise in temperature was read to 0.001° C. on a Beckman thermometer of known heat capacity. Temperature was taken as a function of time, the curve plotted, and allowance made for radiation. A separate determination of the specific heat was made for the most concentrated solution, 41.8 per cent. With this value and the known specific heat of the ethyl bromide as extreme points a curve was drawn through the intermediate percentages, and specific heats taken from this curve for the other solutions. The error thus introduced is negligible for the purpose in hand.

The ethyl bromide was thoroughly dried over fused calcium chloride, and a freshly distilled portion used for each determination. The aluminum bromide was made by conducting bromine

[3] Jour. Russ. Phys. Chem. Soc., *3* 466, (1902).
[4] Berichte, Referate *17*, 163, (1884).

over aluminum turnings in a red-hot combustion tube and redistilling the product from aluminum chips. Only the cleanest fractions were taken. The salt appears snow white in thin layers, but the liquid salt is a very light yellow.

RESULTS.

In Table I below, Column I contains the weight in grams of aluminum bromide taken; Column II, that of the ethyl bromide; Column III, the per cent. by weight of aluminum bromide upon the total weight of the solution; Column IV, the specific gravity of the solution—given with an accuracy sufficient to permit of calculating the position of each solution on Plotnikoff's molecular conductivity curve; Column V, the number of cubic centimeters of solution containing one gram molecule of solution; Column VI, the temperature of the experiment; Column VII, the small calories evolved; Column VIII, the heat of solution for a gram molecule of salt, in small calories; Column IX, the voltage calculated from the heat of solution of a gram equivalent of $AlBr_3$ by the formula,[1]

$$\pi = \frac{H \times 4.24}{e \times 96{,}540}$$

where π = volts; H = heat of solution for a gram molecule; e = valence; 4.24 = electrical equivalent of heat; 96,540 = Constant of Faraday's Law.

TABLE I.

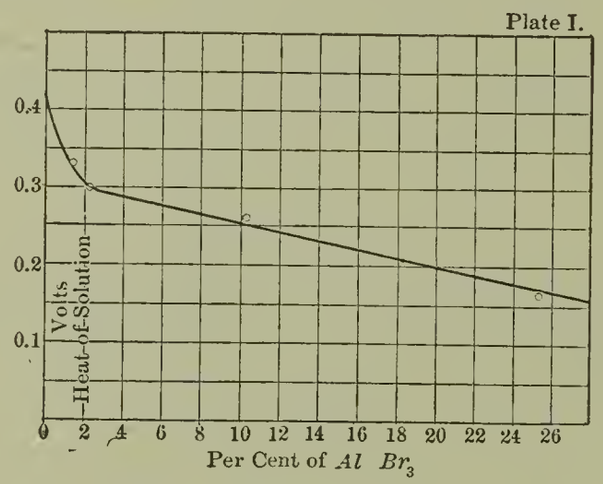
Exp.	I Grams $Al\,Br_3$	II Grams $C_2\,Hs\,Br$	III Per Cent. by Weight	IV Sp. Gr. Sol.	V C. C. Containing 1 Gram Molecule	VI Temp. of Exp.	VII Calories Evolved	VIII H Calories Heat of Solution	IX $\pi = \frac{H \times 4.24}{3 \times 96540}$ Volts from Heat of Solution
1	16.8150	23.5240	41.8	1.67	383	20.2	382.72	6,077	0.088
2	20.5138	34.8272	37.1	1.64	438	20.1	648.99	7,397	0.108
3	18.3423	53.5476	25.5	1.58	664	20.1	794.67	11,540	0.169
4	3.6265	31.9320	10.2	1.46	1793	20.1	241.09	17,750	0.260
5	2.888	126.983	2.23	1.45	8640	18.5	225.87	20,534	0.301
6	0.5541	36.457	1.479	1.45	12,732	19 9	47.93	23,097	0.339

Plate I gives the curve for the variation of voltage (calculated

[1] The term $T\frac{d\pi}{dT}$ is omitted because the temperature coefficient is not known.

from the heat of solution) with the per cent. of aluminum bromide used, as shown by Columns III and IX of Table I. Ordinates are in volts and abscissae in per cent. of aluminum bromide. The sharp rise in the curve between 2.1 per cent. and 0 per cent. indicates that for low concentration we should have a heat of solution corresponding to more than 0.4 volt. Returning now to the values given in the introduction, we note 0.552 volt as the e. m. f. attributable to heat of solution. Against this we may place 0.339 volt as the highest experimentally obtained heat of solution value—for a 1.497 per cent. solution. But the probable exterpolation value for very dilute solution is 0.42 volt. Adding this to 1.748 volts—the pressure necessary to decompose aluminum bromide, as calculated from its heat of formation in the anhydrous condition—gives 2.17 volts, the e. m. f. likely to be

Plate I.



required to deposit aluminum and bromine from an ethyl bromide solution of aluminum bromide. The experimental decomposition point was found to be 2.30 ($\pm$ .02) volts.[1] So the lack of agreement between the decomposition voltage as calculated and that actually found amounts to 0.13 volt, if we use the exterpolation value, 0.42 volt; and to 0.21 volt, using the experimental value, 0.339 volt for the heat of solution.

The theoretical voltage of decomposition, 2.17, calculated from thermal data, is lower than the experimental. Causes contributary to this are, (a) aluminum deposited from ethyl bromide solution reacts upon the solution giving off hydrocarbon gases, and (b) at present it is not generally maintained[2] that electrical deposition is a strictly reversible process.

[1] Loc. Cit.

[2] Zeit. phys. Chem., *12*, 333 (1893); and *13*, 163 (1894).

In the experimental determination of the decompostion point it was found that free bromine came off at the anode.[1]

By means of the single potentials we can now tentatively locate this heat of solution.

TABLE II.

Single Potential in Aqueous $AlBr_3$	Single Potential in $C_2H_5Br + AlBr_3$	Difference due to heat of solution
Al^2 + 1.46 volts	+ 1.10	Cathode 0.36
Br^2 — 1.53 volts	— 1.20	Anode 0.33

From this comparison it seems that the heat of solution is divided between anode and cathode nearly equally, as far as the excess of heat of solution for aqueous over that for ethyl-bromide solution is concerned. Of course this analysis of values rests upon the potential of the normal calomel electrode—sometimes called Ostwald's zero—and a shift in its value, 0.56 volt, will produce a corresponding change here. And it must be considered, too, that decomposition voltage as taken from a current voltage curve is not exact in the second decimal place.

The above considerations show that by use of thermal data one may calculate within rough limits the voltage necessary to decompose aluminum bromide when dissolved in ethyl bromide. And it is shown that aluminum conducts itself as anode in this solution in a perfectly regular manner. The energy considerations which hold for aqueous solution are valid here as well.

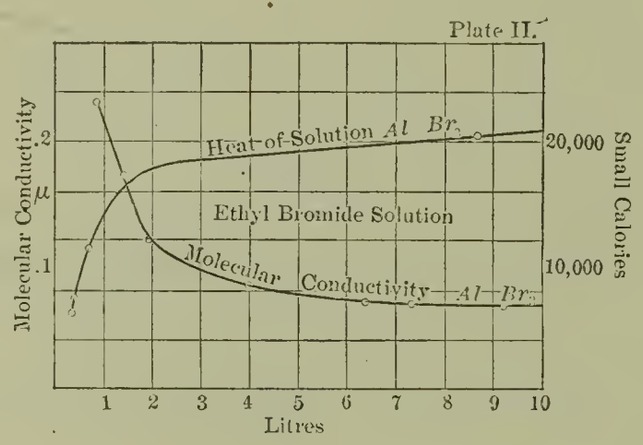
In Plate II the molecular conductivity[2] for $AlBr_3$ in ethyl bromide is plotted as a function of the dilution in liters; and superposed on this curve is the heat of solution from Table I, Column VIII, at various concentrations. Ordinates at the left are in molecular conductivity; at the right, in small calories, and the abscissas for both curves are in liters.

V	M
0.89	0.23
1.44	0.17
1.92	0.12
4.00	0.084
6.36	0.074
7.4	0.071
9.17	0.065
17.9	0.065
40.0	0.082

[1] Loc. Cit.

[2] Molecular conductivity of $AlBr_3$ in ethyl bromide as determined by Plotnikoff (Jour. Phys. Chem. Ref., page 236, 1903).

The heat of solution curve resembles that of sulphuric acid in water, and appears to be quite regular, while the molecular conductivity curve for $AlBr_3$ in Plate II is abnormal. There is, then, no correspondence here between the energy liberated in forming the solution and its peculiar molecular conductivity.[2] Arrhenius has tried to explain why ionization does not always appear to absorb heat. But any explanation of that sort can hardly hold in both these cases cited. The real difficulty lies in the calculation of the molecular conductivity, as I stated in a previous paper.[3] And C. J. Reed[4] has presented this matter clearly: in calculating molecular conductivity (a) we compare the resistance of electrolytes of different cross-section, and (b) no account is taken of the solvent in determining the conduction of the solution, save to subtract the specific conductivity of the solvent in pure condition.



While there is no desire to call in question Gustavson's conclusion that the composition of the solution approaches $AlBr_3C_4H_9$, it is worthy of note that in all the heat of solution experiments carried out, the heat was evolved (after mixing) in a very regular manner and required no long time for the thermometer to reach its maximum; the cooling curve, too, was regular. This means that secondary reactions progress very slowly and are of minor import in connection with the abnormal molecular conductivity curve.

It should be stated here that a 20 per cent. solution of aluminum bromide in ethyl bromide, made up and maintained at 0.5° C.,

[2] Zeit. phys. Chem., *4*, 96 (1889); *9*, 339 (1892); *11*, 174 (1893).

[3] Influence of the Solvent in Electrolytic Conduction. Jour. Phys. Chem., *6*, 554 (1902).

[4] Trans. Am. Electrochem. Soc., Vol IV, 103 (1904). Consult further the views of L. Kahlenberg given in his paper, Recent Investigations Bearing on the Theory of Electrolytic Dissociation. Trans. Faraday Society 1, *1*, 62 (1905).

showed a regular increase in its vapor pressure of 4.44 mm. per minute during the first 50 minutes after mixing; and this rate of increase fell to 3.6 mm. per minute for the next 31 minutes. So it is clear that aluminum bromide acts upon ethyl bromide, evolving a gas even in the neighborhood of zero degrees centigrade. This experiment was made to ascertain whether the vapor pressures of solutions of aluminum bromide in ethyl bromide might not be determined and compared with the conductivity and heat of solution curves. At this temperature the evolution of gas from the solution renders such work futile.

SUMMARY AND CONCLUSIONS.

(1) The heat of solution of aluminum bromide in ethyl bromide has been determined near 20° C. at six concentrations: 1.497 per cent., 23,097 calories; 2.23 per cent., 20,354 calories; 10.2 per cent., 17,750 calories; 25.5 per cent., 11,540 calories; 37.1 per cent., 7,397 calories; 41.8 per cent., 6,077 calories.

(2) It is shown that the voltage required to decompose a solution of aluminum bromide in ethyl bromide, liberating aluminum and bromine, may be roughly calculated by Thomson's formula, using as thermal data the heat of formation of anhydrous $AlBr_3$ plus its heat of solution in ethyl bromide for dilute solution. And the difference between this calculated decomposition voltage and that experimentally obtained[1] is 0.13 volt, or 23.5 per cent. of the total voltage attributable to the heat of solution. But if we take the total voltage of aluminum against platinum in this solution, 2.235,[2] instead of the decomposition voltage (2.30 volts), the agreement is better. The difference then is 0.065 volt, which is 10.8 per cent. of 0.552 volt, the total voltage to be calculated from the heat of solution. The presence of a secondary action at the cathode explains this discrepancy. These results may be taken as indicating that with proper conditions, agreement between decomposition voltage calculated from thermal data and that determined experimentally by electrolysis will be found, provided the same chemical reaction obtain in the thermal and in the electrolytic experiments. In reality the heat of solution curve (Plate I) rises much more steeply than represented, since the layer of solu-

[1] Loc. cit.
[2] Loc. cit.

tion near the cathode is extremely dilute. This would make for better agreement between the calculated and the observed decomposition point.

On the other hand, one may take the ground that the experimentally obtained heat of solution (for 1.5 per cent. solution) is 38 per cent. less than that which was to be expected from the experimental determination of the decomposition point of this solution. And on this basis may maintain that thermal data do not lend themselves to the calculation of decomposition voltage.

(3) The heat of solution when plotted as a function of dilution (Plate II) has much the same form as the heat of solution curve for sulphuric acid in water.

(4) The results stated in 1, 2 and 3 show that the solution of aluminum bromide in ethyl bromide is subject to the same energy considerations as obtain in aqueous solution, although its molecular conductivity curve is radically abnormal. At the same time the molecular formula of aluminum bromide, 11 per cent. in ethyl bromide, was shown[1] to be very nearly $AlBr_3$ by the freezing point method. And this concentration lies in the region of rapid deviation of molecular conductivity from the trend of curve required by the theory of electrolytic dissociation.

(5) The single potentials of aluminum and of bromine in aqueous aluminum bromide solution and in ethyl bromide solution of the same solute are compared. And it is shown in a tentative analysis that the heat of solution when expressed as volts is very nearly evenly parted between the anode and the cathode.

I wish to thank Prof. L. Kahlenberg for facilities and for kindly criticism of this work.

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DISCUSSION.

Prof. T. W. Richards, Harvard University: In this paper Dr. Patten speaks of having used Helmholtz's formula in calculating his results. I ask for information. It seems to me he has rather

[1] By Plotnikoff, loc. cit.

used the equation of Berthelot or Thomson. That is to say, he has confounded total energy and free energy. Now if it is true that in this particular case the total energy is equal to the free energy change, that is, that the cell has no temperature coefficient, it is an interesting case and one which is well worth while studying further on this account. On the other hand, in view of the fact that Dr. Patten acknowledges decomposition at the electrodes, the conditions are uncertain, and the investigation as presented to us is an interesting beginning rather than a complete treatment of the subject. Being given as a complete treatment, a portion of it appears to be distinctly misleading. I should like to receive an answer to this question.

DISCUSSION.

(*Communicated after the meeting by Prof. H. E. Patten.*)

Professor T. W. Richards has asked me to explain the reference to Helmholtz's equation,

$$\Pi = \frac{Q \times 4.24}{\Sigma \times 96{,}540} + T\frac{d\Pi}{dT}$$

in this paper. His request is natural, since no mention of the temperature coefficient is made in the paper as originally presented. This leads one to infer either that the cell has no temperature coefficient, or that free and bound energy are not clearly separated in the author's mind.

The fact is, the temperature coefficient has not been determined as yet. The use of heat of solution plus heat of formation in calculating the voltage of decomposition is so evidently a rough approximation that I had not supposed anyone would think I looked upon it as final, or as a complete treatment. In paragraph 2, under summary and conclusions, the phrase reads "may be *roughly* calculated."

When one drops the term $T\frac{d\pi}{dT}$ from Helmholtz's equation the remainder becomes Thompson's formula. But in this paper I referred to the use of Helmholtz's formula because I had been

thinking in terms of that formula, and omitted the temperature coefficient only until it should be determined experimentally. The lack of clearness thus produced had not occurred to me, and I am indebted to Professor Richards for calling attention to it.

In the absence of an experimental determination of the temperature coefficient, it is of interest to calculate its probable magnitude and sign. In article 2 under summary and conclusions, + 0.13 volt is given as the discrepancy between the calculated and the experimental decomposition voltage. This value corresponds to the term $T\frac{d\pi}{dT}$. T is 20° + 273°, or 293°; so $\frac{d\pi}{dT} = +\ 0.000443$ volt per 1° C., a value rather high but not improbable.

The review of this paper given in Electrochemical and Metallurgical Industry, Vol. III, page 179, quotes Dr. Richards as objecting that a complete treatment of the case would involve far more experimental work. On careful rereading I find nothing in my paper to warrant the assumption that I consider the problem as finished. I have used the words "rough" and "tentative" in the two critical places, and have discussed the results in an impartial manner from several standpoints. It seems to me that this review gives a false impression both of Professor Richards' attitude toward my paper, and of the paper itself. This statement is based upon a typewritten report of Dr. Richards' discussion at the meeting and upon private correspondence with Dr. Richards himself. It seems there is no clash in our ideas.

Laboratory of Physical Chemistry,
University of Wisconsin, Madison.

A paper read at the Seventh General Meeting of the American Electrochemical Society, held at Cambridge, Mass., April 26, 1905. President Carhart in the chair.

THE INTERDEPENDENCE OF THE ATOMIC WEIGHTS AND THE ELECTROCHEMICAL EQUIVALENTS.

By Arvid Reuterdahl.

It is a well-known fact that a definite relation exists between the atomic weights and the electrochemical equivalents of the elements. This knowledge has served as a basis for a limited class of theoretical and practical electrochemical computations. No deeper significance seems to have been attributed to the matter by writers upon the subject. The data which are fundamental to the present discussion are found in the accompanying table. Using

Elements	Symbols	Valencies	η Electrochemical Equivalents per Unit Valence	ρ Ampere Hours per Gram per Unit Valence	θ Atomic Masses
Hydrogen	H	1	.00001044	26.5957	1.000
Carbon	C	4	.0001240	2.2401	11.91
Nitrogen	N	3	.0001452	1.9135	13.93
Oxygen	O	2	.0001658	1.6756	15.88
Sodium	Na	1	.0002388	1.1632	22.88
Magnesium	Mg	2	.0002516	1.1040	24.18
Aluminium	Al	3	.0002808	.9891	26.9
Chlorine	Cl	1	.0003672	.7565	35.18
Potassium	K	1	.0004052	.6855	38.86
Calcium	Ca	2	.0004154	.6687	39.8
Manganese	Mn	2	.0005700	.4873	54.6
Iron	Fe	2	.0005804	.4788	55.5
Nickel	Ni	2	.0006080	.4568	58.3
Copper	Cu	1	.0006586	.4218	63.1
Zinc	Zn	2	.0006774	.4100	64.9
Bromine	Br	1	.0008281	.3354	79.36
Silver	Ag	1	.0011180	.2485	107.12
Tin	Sn	2	.0012328	.2253	118.1
Antimony	Sb	3	.0012471	.2227	119.3
Iodine	I	1	.0013140	.2114	125.9
Platinum	Pt	2	.0020188	.1376	193.3
Gold	Au	3	.0020427	.1360	195.7
Mercury	Hg	1	.0020719	.1340	198.5
Lead	Pb	2	.0021436	.1296	205.35

the values of η, the electrochemical equivalent per unit of valence, as ordinates and the corresponding values of θ, the atomic weights of the elements, as abscissas, a straight line (Fig. 1) is obtained which corresponds to the equation:

$$\eta = K\theta \tag{1}$$

where K is the constant 0.00001044.

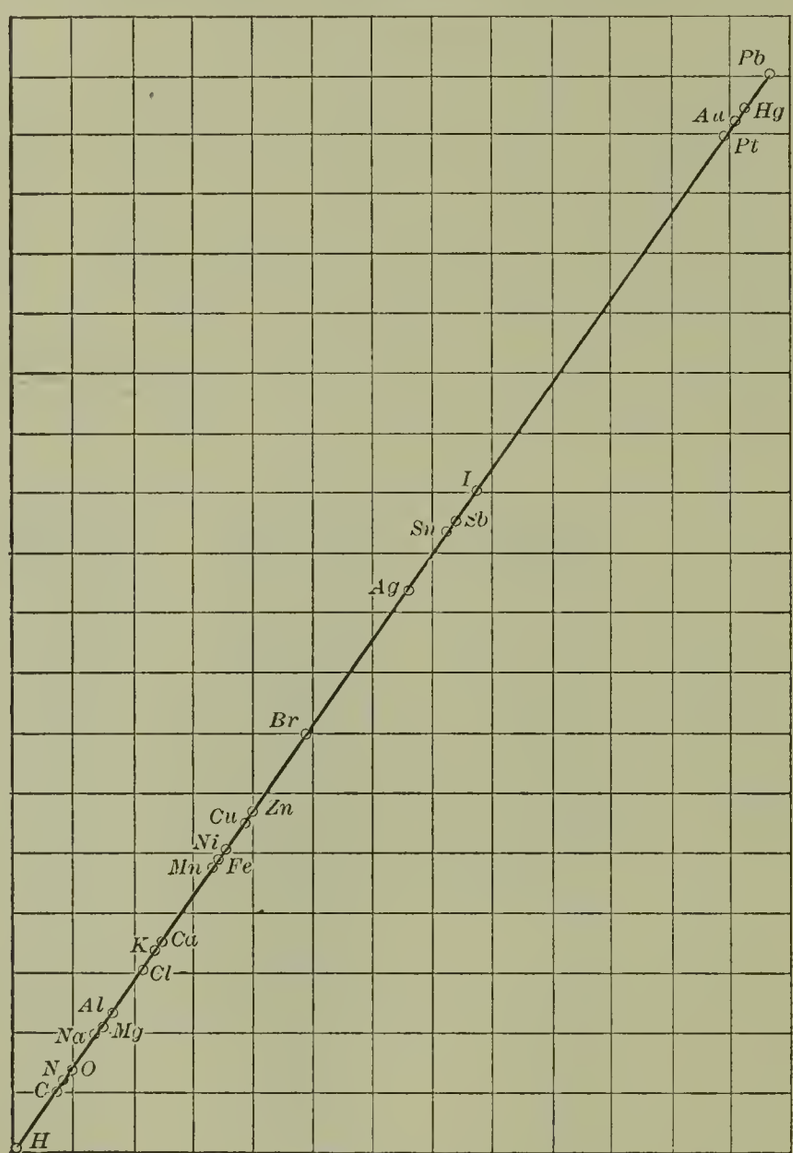


Fig. 1

If ρ be the number of ampere hours per gram per unit of valence, it is found that, on account of the large differences between ρ for Hydrogen and ρ for the other elements, it is not advisable to plot the values of ρ as ordinates and the corresponding values of θ as abscissas. It is far more preferable to refer the values of ρ and θ to a system of polar co-ordinates. By this means the relations between these can be depicted in a very effi-

cient manner. The values of ρ, then, become radii vectores while the corresponding values of θ are proportional to the vectorial angle. The curve thus produced constitutes an Hyperbolic Spiral. The arc described by the radius vector of any point on this curve is equal to C, a constant quantity. For an infinite value of ρ this arc becomes perpendicular to the polar axis AB (Fig. 2), and hence the line MN parallel to the polar axis AB at a distance C above it is an asymptote to the infinite branch of the curve. This curve is completely represented by the equation:

$$\rho\,\theta = C \tag{2}$$

which can be put into the form

$$d\theta = -C\frac{d\rho}{\rho^2} \tag{3}$$

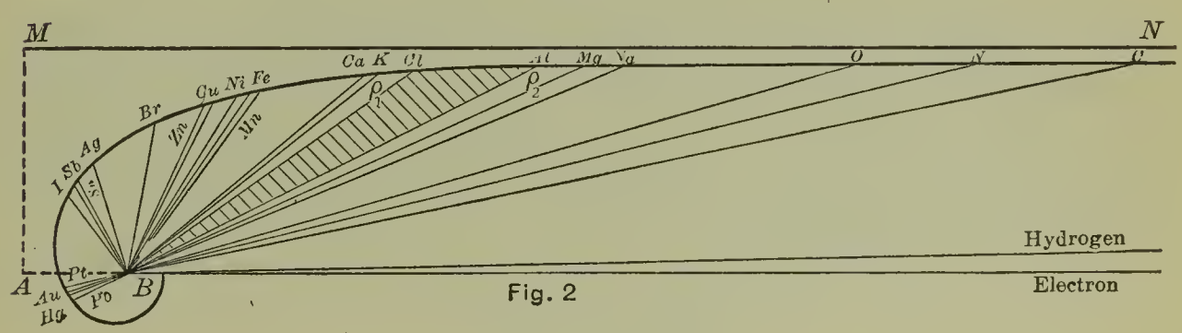


Fig. 2

The expression for the area enclosed between the curve and any two particular radii vectores as ρ_1 and ρ_2 (Fig. 2) will have the general form:

$$\tfrac{1}{2}\int_{\rho_1}^{\rho_2} \rho^2\, d\theta$$

Making use of equation (3) this general expression becomes:

$$\tfrac{1}{2}\,C\int_{\rho_1}^{\rho_2} d\rho$$

which reduces to

$$\tfrac{1}{2}\,C\,(\rho_2 - \rho_1) \tag{4}$$

This expression is of the same form as the general expression derived in thermodynamics for the work done when a system passes from the state (1) to the state (2).

In the general thermodynamical expression,

$$W = U_2 - U_1$$

the increase of internal energy is represented by $U_2 - U_1$, and its value is determined by the initial and final values of the variables involved, which in thermodynamics are pressure, volume, and temperature.

The general similarity of the equation

$$\rho\,\theta = C$$

to the law of Boyle and Mariotte is, indeed, noteworthy. The mathematical development of the present equation along the lines of thermodynamics is clearly possible.

Let us now imagine the atom as a spherical shell which is capable of expanding and contracting with pressure. We shall also assume that the volume of this spherical shell is, at all times, proportional to the mass of the atom. Hence V, the volume of the spherical shell, is proportional to θ the mass.

If a change of volume from V_1 to V_2 is effected, the decrement in volume is proportional to the corresponding decrement in mass occasioned by a change in mass from θ_1 to θ_2. This is evident from our assumptions. The work done in effecting this change is given by the expression:

$$\tfrac{1}{2}\,C\,(\rho_2 - \rho_1)$$

Hence the work done is proportionate to the change of state from ρ_1 to ρ_2 or to the increment of ρ. The quantity of electricity necessary to liberate a unit mass of θ_2 will then be given by ρ_2.

Now as mass attraction is expressed by $k\,\frac{m\,m^1}{d^2}$, it follows that a change in mass will be accompanied by a proportionate change in the value of $k\,\frac{m\,m^1}{d^2}$. The magnitude of this quantity pertaining to the spherical shell at any particular instant will be spoken of as its gravitational state. For a similar purpose we will use the corresponding term electrical state. A decrement in the gravitational state of θ will be accompanied by an increment in the ratio of the electrical state e to the gravitational state θ. On the other hand, any increment in the gravitational state will likewise mean a decrement in the ratio e/θ. The analogy to the transformation of kinetic energy into potential energy is striking. If a body is projected vertically upwards

from a position L_1 to a position L_2, work is done against gravity and kinetic energy is transformed into potential energy. As the kinetic energy decreases so does the ratio between the potential and kinetic energy increase. As far as this particular change is concerned the body will possess a maximum of potential energy and a minimum of kinetic energy when at the point L_2. This potential energy can be again transformed into kinetic energy by allowing the body to fall through the distance L_2L_1. Similarly in compressing θ we do work against gravitational force and an increment in the value e/θ occurs. Furthermore, just as kinetic energy is ultimately not different in its real nature from potential energy, so gravitational potential must be of the same order as electrical potential.

The validity of the above conclusions may be demonstrated by the consideration of a concrete case.

Suppose that we submit a spherical shell having a volume which is proportionate to the mass of the hydrogen atom to compression until its volume is $\frac{1}{1000}$ of its initial volume. The final volume thus produced by compression is therefore proportionate to the mass of the corpuscle or electron. The ratio of the initial to the final volume would be expressed by

$$\theta_E = \tfrac{1}{1000}\,\theta_H$$

where θ_E is assumed to be equal to the mass of the negative gaseous ion or electron, and θ_E is the mass of the hydrogen atom. In effecting the compression work must be done and gravitational state will be transformed into electrical state. The resulting electrical state for the unit of mass should be given by the expression:

$$\rho_E\,\theta_E = C$$

Now since $3600\ \rho\ \eta = 1$ we obtain

$$\eta = K\,\theta \quad \text{where}$$
$$K = \tfrac{1}{3600}\,C$$

$$\text{For } \theta_E = \tfrac{1}{1000},\ \eta = \frac{0.00000001044}{3 \times 10^9}$$

which reduces to 0.348×10^{-17} grams per each electrostatic unit.

From the value of $\frac{e}{m} = 3 \times 10^{17}$ found by J. J. Thomson,[1]

[1] J. J. Thomson, "Electricity and Matter," p. 110, 1904.

m, the mass of the negative ion (corpuscle or electron), is equal to 1.13×10^{-27}. Here e is the charge on the corpuscle in electrostatic units. Substituting these values in $N = \eta / m$, where N is the number of corpuscles for one electrostatic unit, we find:

$N = 3.07 \times 10^{+9}$, and since $Ne = 1$, it follows that $e = 3.2 \times 10^{-10}$ electrostatic units.

This is very concordant with the value of e obtained experimentally by H. A. Wilson.[2]

$$e = 3.1 \times 10^{-10} \text{ electrostatic units;}$$

and by J. J. Thomson.[1]

$$e = 3.4 \times 10^{-10}.$$

Now, as the charge carried by the hydrogen ion in electrolysis has been found to lie between the values of 6.1×10^{-10} and 1.29×10^{-10}, we are justified in assuming with J. J. Thomson[1] that the charge carried by the corpuscle is equal to the charge carried by the hydrogen ion in the electrolysis of solutions.

The value of e obtained by the writer follows, then, from the assumption that when a spherical shell, having the properties previosuly defined, is compressed, then the change of gravitational and electrical state takes place according to the law that $\rho\,\theta$ is a constant quantity. The only extraneous value introduced was the value of m, the mass of the negative gaseous ion.

That the value of e is a constant for all ions will now be shown. For this purpose we shall consider the equation:

$$N = \eta / m$$

If it be assumed that $\theta = \lambda\, m$ where λ is a constant, then, knowing that $\eta = K\,\theta$ we obtain by introducing these expressions into the above equation:

$$N = K\,\lambda$$

For $K = .00000348 \times 10^{-9}$, and $\lambda = .884 \times 10^{24}$, we obtain $N = 3.07 \times 10^{+9}$.

This fact can then be expressed as a general law:

"The number of ions, whether gaseous or liquid, liberated by a given quantity of electricity is a constant, independent of the kind and mass of the ion."

[1] J. J. Thomson, "Conduction of Electricity Through Gases," p. 129, 1903.
[2] H. A. Wilson, Phil. Mag. April 1903.

Moreover, since $Ne = 1$, it follows that $e = 1/K\lambda$, which for the above values of K and λ gives $e = 3.2 \times 10^{10}$ electrostatic units.

The following general law then follows as a corollary to the first:

"The charge carried by a free ion, whether gaseous or liquid, is a constant quantity independent of the kind and mass of the ion."

We are, therefore, justified in assuming that if particles smaller than the corpuscles should ever be discovered, we would know in advance the charge carried by such a particle. Moreover, if e is a constant quantity, it follows that the value e/θ depends only upon the value of θ. Therefore, if the ratio $\frac{\theta_1}{\theta'}$ between any two particular atoms is represented by μ then

$$\frac{e'}{\theta'} = \mu \frac{e_1}{\theta_1} \tag{5}$$

When a molecule which is composed of a number of atoms is decomposed by the electric current it cannot be split into more than two parts, for the number of ions liberated by a given quantity of electricity is a constant. Consequently, if a molecule is made up of more than two atoms, one of the ions must contain more than one atom. Hence, when water is electrolyzed by the electric current there are two ions formed, H and OH. Suppose that a quantity of electricity Q is necessary to liberate 1 gram of hydrogen, then Q will liberate only 7.94 grams of oxygen. This is evident because the quantity of electricity e necessary to liberate one H ion also liberates the same number of OH ions, or *one* only. In order to liberate one oxygen atom an additional quantity of electricity e must therefore be similarly applied to the OH ion. Hence the quantity of electricity Q can liberate only half as many oxygen atoms as hydrogen atoms. This is, then, the real significance of the fact that oxygen is here divalent.

Let us revert once more to the conception of a compressible imaginary spherical shell whose successive volumes V_1 and V_2 are always proportionate to the corresponding masses θ_1 and θ_2. Let us also imagine another spherical shell which is allowed to expand in strict accordance with the same fundamental assumptions which govern the phenomenon of compression. Suppose

that the second spherical shell has an initial volume V′ which may expand to a volume V″, and that this increment in volume is proportionate to a corresponding increment in mass from θ' to θ''. Finally, assume that the two shells V_1 and V′ are so intimately related that when V_1 is compressed a flow of mass from θ_1 to θ' sets in and continues with the pressure until θ^2 equals θ'' This would correspond to the flow of liquid in intercommunicating vessels from a higher to a lower level until equalization and equilibrium is produced. For convenience we shall regard the electrical state as well as the gravitational state as partaking of the nature of mass. That we are justified in using the term *"electrical mass"* follows from the researches of Kaufmann[1] when taken in conjunction with the calculations of Sir Oliver Lodge.[2]

Furthermore, a charge of electricity in motion, regarded from the standpoint of the electromagnetic theory, behaves as if it possessed mass. This has been shown by J. J. Thomson,[3] Heaviside,[4] and Searle.[5]

Let Fig. 3 be a graphical representation of an undisrupted molecule composed of the two ions θ_2 and θ''. We shall tentatively assume that the ions which constitute a molecule have the same temporary mass, and that this is a distinctive feature of the molecular condition. In Fig. 3, θ_2 is therefore supposed to be equal to θ''. The respective electrical charges or masses are represented by the dotted circles e_2 and e''.

Upon the application of an electromotive force to the system a flow of electrical mass from e'' to e_2 begins and continues until e_2 becomes equal to e''. But it has already been shown that when a molecule is electrolyzed the charge carried by each of the free ions is a constant quantity. Hence at the moment of disruption e_2 must equal e″. This condition is shown graphically in Fig. 4, where e_1 equals e′. We have found (equation 5) that

$$\frac{e'}{\theta'}\,\mu = \frac{e_1}{\theta_1}$$

where μ is the ratio $\frac{\theta_1}{\theta'}$. Consequently when e_1 equals e', then $\theta_1 = \mu\theta'$ and the masses of θ_1 and θ' are again the free atomic masses.

[1] Kaufman, Phys. Zeit. *4* No. 1 b, p. 54, 1902.
[2] Lodge, Nature, June 11, 1903.
[3] J. J. Thomson, Phil. Mag. April, 1881.
[4] Heaviside, Collected Papers, Vol. 2, p. 514.
[5] Searle, Phil. Mag. October, 1897.

On the other hand, when $\frac{e'}{e_1} = \mu$, then $\theta_1 = \theta'$. This is the condition represented in Fig. 3 where $\theta_2 = \theta''$.

Simultaneously with the change in the system from the state indicated in Fig. 3 to the state shown in Fig. 4 there occurs a displacement of A to A' and B to B'. The value of $A'B'$—AB.

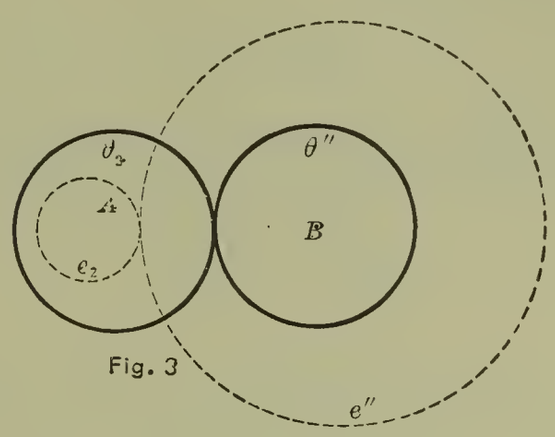


Fig. 3

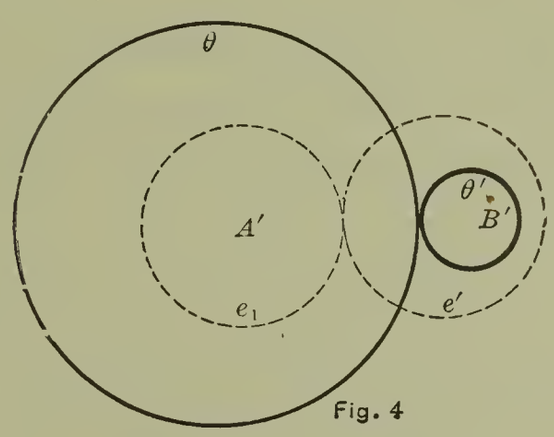


Fig. 4

will therefore be a constant quantity for any particular type of molecule in any one definite system. The value AB will depend upon the actual physical relation between θ_2 and θ''. The only possible assumption concerning the physical relation between θ_2 and θ'', the ions of the molecule, are:

First.—That they never come into actual contact.

Second.—That they are contiguous.

Third.—That they partially envelop each other.

Fourth.—That they are absolutely concentric.

The initial value of AB, therefore, depends upon whichever of these suppositions proves to be the actual condition for the molecular state. Similarly the value $A'B'$ will depend partially upon the above assumptions, but principally upon the value of θ_1

and θ' at the moment of disruption. At this instant e is the same for all ions, hence it follows that the decomposition of a molecule cannot take place without involving a decomposition constant which undoubtedly has a definite relation to the value $A'B'—AB$. If this value be represented by $\triangle$ and E be the *decomposition-voltage* of the molecule, then

$$E = f \triangle$$

If gravitational mass be regarded as involving attraction while electrical mass involves repulsion, it would follow that if

$$\frac{e_1 \times e'}{d^2} = \frac{\theta_1 \times \theta'}{D^2}$$

then a condition of neutral equilibrium would exist. Even if the value $\frac{e_1 \times e'}{d^2}$ never increased beyond this point and thus became greater than $\frac{\theta_1 \times \theta'}{D^2}$, then the subsequent behavior of the ions would be determined solely by the remaining factors of the system. If, however, the value $\frac{e_1 \times e'}{d^2}$ became greater than $\frac{\theta_1 \times \theta'}{D^2}$, then the remaining factors would exercise merely a partial influence on the subsequent career of the ions. When decomposition sets in, then the ions are free to migrate and to effect the requisite exchanges of electrical mass which may be demanded by the particular system.

Gravitational and electrical mass may then be regarded as the two aspects in which mass manifests itself to us. On the one hand we have attractions, kinetic energy, absorption and integration; on the other hand we have repulsions, potential energy, self-conservation and differentiation; yet these are merely the two modes in which actual mass interactions take place.

The conservation of mass and therefore the conservation of energy follows as a direct consequence from the previous considerations.

DISCUSSION.

PRESIDENT CARHART: Are there remarks to be made upon this paper?

PROF. W. S. FRANKLIN: Professor Reuterdahl has evidently taken a great deal of pains with his paper, and I think that it is right that the paper should receive some discussion. I must say that from what Professor Richards has said, and from two or three statements that catch my eye as I glance the paper over, I feel a little doubtful of its value as a precise contribution to the theoretical branch of electrochemistry.

DISCUSSION.

(*Communicated by Prof. Arvid Reuterdahl after adjournment.*)

The pioneer investigations of Faraday brought out the significant facts that in the electrolysis of liquids, "the chemical power of a current of electricity is in direct proportion to the absolute quantity of electricity which passes,"[1] and, "only single electrochemical equivalents of elementary ions can go to the electrodes, and not multiples."[2]

Recent interest has centered about the discharge of electricity through gases. The researches of J. J. Thomson, H. A. Wilson and Kaufmann have shown that the charge carried by the negative gaseous ion is equal to the charge carried by the hydrogen ion in the electrolysis of solutions.

In the preceding exposition a general expression has been developed which contained quantities so related that the charge or electrical mass associated with the actual mass of any ion, regardless of its source, can be determined. We have embodied the work of Faraday and Thomson in a single conception which expresses the relation between gravitational and electrical masses for any material particle whatsoever liberated by electricity.

The *price of liberty* which must, so to speak, be paid by any ion whatsoever is a constant quantity, $e=3.2\times10^{-10}$ electrostatic

[1] Michael Faraday, "On Electrochemical Decomposition" ("The Fundamental Laws of Electrolytic Conduction," Harper's Scientific Memoirs), p. 37.

[2] Michael Faraday, Ib., p. 39.

units. The value e may be called the *mobile differential* of electrical mass. This *mobile differential* e may be regarded, on the one hand, as existing, temporarily during decomposition, as an increment in electrical mass upon one of the ions, over and above the electrical mass absorbed by this particular ion while being incorporated into the molecular organization; on the other hand, it may be looked upon as being that definite amount of electrical mass which must always be interposed between the ionic shells before disruption can take place. This *mobile differential* is given up to the electrode, and then passes around the circuit again to perform the same function in an unbroken cycle. This constitutes the flow of an electric current. Simultaneously with this occurrence the ion gives back the surplus of electrical mass which it acquired from the other ion when the molecule was formed and the ionic masses themselves become atomic or molecular.

Moreover, as this *mobile differential* is the same in all the varied cases of ion liberation it follows that the work done in developing and introducing it into the molecular organization is, ultimately, a function which depends for its value upon the relative masses of the ions constituting the particular molecule. The decomposition constant which pertains to every complete molecular system is mathematically comparable with the work thus expended.

A paper read at the Seventh General Meeting of the American Electrochemical Society, held at Cambridge, Mass., April 26, 1905. President Carhart in the chair.

NOTE ON THE UTILIZATION OF BLAST-FURNACE GASES IN CONNECTION WITH THE ELECTRIC SMELTING OF IRON.

By Auguste J. Rossi.

The utilization of the waste gases of the blast furnace to generate power with gas engines has passed the stage of experiments, and, after having received in Europe the consecration of practice by the establishment of nearly 200,000 HP. already, has begun to receive serious attention in this country, where large steel works are contemplating to give it, or are actually taking steps to give it, important application.

The production of electrical energy or its equivalent in heat at a moderate cost, by means of gas engines, opens possibilities for electro-metallurgy in general and in particular for the manufacture of steel of which the importance cannot be ignored. This question of electric smelting of steel has been discussed by competent writers here and abroad, and it is not our intention to recall what has been written on this subject. But the fact that electricity, the basis of such manufacture, can be obtained from what was before a waste product, and obtained in proximity to the blast furnace, simultaneously with the production of pig iron, and this in such amount as could hardly be anticipated, may remove from this industry the serious objection to its development, that of obtaining economically a sufficient electric horse power independently of the more favored conditions of certain localities. It has been shown and we believe it is generally admitted that steel, electrically obtained, possesses superior qualities to those of good open-hearth steel and is nearly as good as if not equal to crucible steel. For the manufacture of ferro metals or metals extensively used now for the treatment of carbon steel—of special steels so much looked for at present, we may find in the utilization of the blast-furnace gases the elements of a new and profitable industry and the satisfactory solution of an important

problem. It is not then irrelevant to examine to what extent such wasted power can be created from these gases, and, as it obviously bears a direct relation to the surplus that can be made available for other purposes than the requirements of a blast-furnace plant, such as heating and compressing the blast and auxiliary power for pumps, hoists, and, in general, labor-saving machinery, to examine also what the total amount of these gases may be in the different conditions of the working of a blast furnace.

The amount of gases per ton of iron produced will vary greatly from one furnace to another, with the consumption of coke per ton of metal, temperature and pressure of blast, and also with the composition of the ores smelted. It is large in all cases, but what we desire to show particularly in the following is that, whatever improvements have been already realized or can legitimately be expected in the future blast-furnace practice, tending to reduce to a minimum the amount of fuel per ton of iron, this amount of gases and consequently the available surplus is not necessarily or only, at least, in direct proportion to the fuel consumed. That, in fact, it cannot very well be below a figure which, even taken as a normal basis, represents as heat energy such an enormous amount of horse power disposable over the requirements of the blast furnace, that the results are still sufficient to satisfy the most sanguine expectations.

As utilized now in blast furnaces to heat the blast and generate steam under boilers, fully one-half of the total amount of gases (52 to 62 per cent.) per ton of iron is wasted. Calculations made by different metallurgists show that this waste, for a production of 20,000,000 tons of pig iron in a year (2,280 tons per hour) (expected this year in the United States, amounts, according to the weight of gases assumed by the writers, in different conditions) to not less than 1,000,000 to 1,200,000 HP. per hour by the most conservative estimate, and may reach as high as 2,000,000 HP. per hour.

These gases have, indeed, a heat value per HP. which is now admitted to be not far from 1,280 thermal units, so that for a production of some 10,000 units of gases per ton of iron, a rather small figure, as we will see, we could count on 12,800,000 thermal units, of which half at least (say 52 per cent., or 700,000

thermal units) would be available for creating power. As the duty of a gas engine is now readily guaranteed by builders to be one effective HP. per 10,000 thermal units in the gases (efficiency 25 per cent.; 1 HP. hour = 2,545 about thermal units), this gives us a surplus of 700 HP. per ton hour, which, for, say: 2,240 ton hours, gives 1,568,000 HP. hour. For a consumption of coke of 2,240 pounds per ton of iron, which is now about a normal average, it is considered that 14,000,000 thermal units can be assumed as the heat value of the gases. If we take only 52 per cent. of this as available surplus, as some conservative estimates do, we come to 728,000 thermal units, corresponding to 728 HP. per ton hour (1,630,700 HP. hour for 2,240 tons).

Even if we assume only 9,000,000 thermal units as heat of the gases, as it has been done by some writer for an exceptionally low consumption of coke, we come still, counting on a surplus of 52 per cent. only, to 468 HP. hour available per ton, or for 2,240 tons per hour, to 1,048,320 HP. hour. This figure we consider as much too low, as we will see, even for a consumption of coke of only 1,700 lbs. per ton of iron (1,726 lbs. have been recently secured in a memorable run of Mr. Gailey under special conditions). Hence, as we have said before, 1,000,000 HP. hour, as surplus, may be considered as a minimum estimate. The quantity of fuel burnt in a given time in a blast furnace has certainly a direct influence on the total amount of gases, but it would be a mistake to conclude *a priori,* that *a smaller amount of coke* per ton of iron necessarily gives *a smaller weight of gases.* As it is, with blast at 704° C., gases escaping at 250° C., with a consumption of coke of 2,240 lbs. per ton of iron, as at the Clarence Works, England, the weight of gases per ton of metal is given by Lowthian Bell at 119.17 cwt. This at 112 lbs. per cwt. gives 13,350 lbs. of gases per ton in round numbers. With such ores as were used in the Pittsburgh Works (Edgar Thomson) with blast at 593° C. and gases at 171° C., the weight of gases per ton of iron is given by L. Bell as 100.10 cwt., or 11,200 lbs., for a consumption of coke of 1,881 lbs. per ton or iron.*

The remarkable run made by Mr. Gailey recently, in the Isabella Furnace, by his method of blowing air dried artificially

* NOTE.—The Iron and Steel Institute in America in 1890. Special volume on the manufacture of pig iron (L. Bell) p. 171.

by means of an ice machine, instead of moist air, has given him, indeed, the low figure of 1,726 lbs. (average) of coke per ton of iron. Were this practice to be generally adopted and this consumption of fuel or even a lesser amount become the rule in our best blast furnaces, *it does not follow* that, *with ores* similar to those Mr. Gailey has smelted, the amount of gases expected would be necessarily smaller than the figures given above by Lowthian Bell. His run demonstrates this plainly, and it is on this point that we desire to call attention.

We find in Mr. Gailey's paper, which has appeared both in the Proceedings of the American Institute of Mining Engineers, Lake Superior Meeting, September, 1904 (Bi-monthly Bulletin, January 15, 1905), and of the Iron and Steel Institute, New York Meeting, November, 1904, the following data on which we can base a calculation. The blast furnace gases contain *carbon* in the state of CO_2 and CO, and *nitrogen* with a small quantity of hydrogen, which we can neglect, as it does not practically affect the result. The carbon is supplied by the fuel, the oxygen and nitrogen by the blast, but a part of the oxygen comes also from the reduction of the oxide of iron of the charges. Neglecting such oxygen as may be furnished by silica reduced to silicon or phosphoric anhydride to phosphorus, as it is mostly compensated by the carbon dissolved in the metal, the weight of the gases per ton is then composed of 1° carbon of fuel, 2° oxygen of the ores, 3° CO_2 from the decomposition of the limestone, 4° weight of blast per ton.

Mr. Gailey, in the paper mentioned (Am. Inst. Min. Eng.), gives the following figures:

Page 20. Charges: 10,200 lbs. coke.
24,000 lbs. ore.
6,000 lbs. stone.

Production in 24 hours, with dry air, average 447 tons.

Average coke per ton of iron, 1,726 lbs.

Average ore mixture, 53.50 per cent. metallic iron (p. 19).

Ashes of coke (p. 19), 10.50 to 12.50 per cent; average 11.50 per cent.

The blast, before the air was dried, was blowing at the rate of 40,000 cubic feet per minute; when the air was dried, at the rate of 34,000 cubic feet, or some 6,000 cubic feet less (p. 23).

34,000 cubic feet of air per minute give 2,623 lbs. blast per minute, or 157,380 lbs. per hour. The production being 447 tons a day, this gives 18.6 tons per hour, with 157,380 lbs. of blast, or 8,460 lbs. of blast per ton of iron.

The coke containing 11.50 per cent. of ashes, this gives practically 88.50% carbon; the ores (hematites Fe_2O_3) contained 53.50% Fe. = 76.43 Fe_2O_3, or 22.90% oxygen.

The charges would give, at 53.50% Fe, 12,840 lbs. iron. Assuming 1% Si (Mr. Gailey's figure) and some 3% carbon, etc., or 96% Fe in the pig metal, 12,840 lbs. iron from the charges represent 13,375 lbs. (nearly 6 tons—5.96 tons) of pig iron for 10,200 lbs. coke; that is, 0.762 lb. coke per pound of metal, or, for one ton, 1,706.88 lbs. coke, which corresponds well for these charges to Mr. Gailey's figures, as given in his table (p. 20), figures of which the average is 1,726 lbs.

No analysis of the limestone is given, but assuming a good calcite of 96% carbonate, this gives us 42% CO_2 in the stone. We have then:

10,200 lbs. coke × 0.885 carbon....	8,927 lbs. carbon in fuel
24,000 lbs. ore × 0.229 oxygen.....	5,496 lbs. oxygen in ore
6,000 lbs. stone × 0.42 CO_2.....	2,520 lbs. CO_2 in stone
Total	16,943 lbs. of gases

for 6 tons of metal obtained from these charges or 2,824 lbs. of gases per ton of metal on the score of these items. If we add the 8,460 lbs. of the blast per ton we come to a total of 11,284 lbs. gases per ton of metal, that is, with only 1,706.88 lbs. of coke; the same amount of gases practically as given by L. Bell for the Edgar Thomson furnace, with moist air, for a consumption of 1,881 lbs. of coke. This calculation shows that, as we have said before, the amount of coke is not necessarily a criterion of the amount of gases, though it certainly enters in each calculation as an element, but that the composition of the ore smelted has a great deal of influence.

According to the latter, more or less limestone will be required giving out CO_2 in the gases, and we can not conceive a blast furnace smelting chemically pure oxide of iron. It is not within the province of this article to discuss what might be, theoretically, the minimum of gases in a furnace working with such pure ores.

It may be sufficient to say that if the ore is richer and per cent. of gangues is low, it will contain more oxide of iron, more oxygen, and will require more carbon for the reduction. As the heat necessary to reduce 1 Kg. of iron from its oxides, to impregnate it with carbon, silicon and phosphorus, and to melt the product represents *several times* the number of calories required for the gangue of the ores and charges to be transformed in slag and melted and for its volatile matters to be gasified, for these reasons, with such *richest ores* as we can practically assume would be smelted, it is not likely that this amount of gases could fall to less than some 8,000 lbs. to 9,000 lbs. per ton of iron, even were the consumption of coke to fall as low as 1,500 lbs. or thereabout.

The figure of 9,000,000 thermal units per ton, assumed by some writers as *the total heat of the gases* for a consumption of 1,700 lbs. of coke, would correspond at a heat value of these gases of 1,280 thermal units per lb. to only 7,000 lbs. of gases per ton of iron, a figure difficult to establish in the ordinary condition of ores; at any rate, we have seen from Mr. Gailey's remarkable run that, even with an amount of coke of only 1,706.88 lbs. per ton, as calculated from his charges, we had still over 11,000 lbs. of gases. But let this figure of 9,000,000 thermal units, as total heat of the gases per ton of iron, stand as it is, and let us utilize as available, as the same writer says, only 52 per cent. of it, or 468,000 thermal units; at 10,000 thermal units per every effective HP. hour in gas engines we come to his figure, 468 HP. hour as available surplus *per ton,* or, for 2,240 ton hours, to over 1,000,000 HP. hours surplus. We consider ourselves justified, then, in conclusion, to assume that this figure is the minimum possible in the best previsions of the blast-furnace practice of the future as to consumption of coke per ton of iron and best condition of ores and steel. It is one which, if only but partly utilized, opens new and great possibilities for electric smelting.

DISCUSSION.

President Carhart: Are there any remarks on this paper?

Mr. E. R. Taylor: It was my pleasure about two years ago to visit the iron works formerly run by George Stephenson (inventor

of the locomotive), in which was a gas engine run by the waste gases from their blast furnaces. It was doing very successful work, and there is no question of the very important future in the use of blast furnace gases for running gas engines.

In this connection I would make the remark that improvements in the last few years with reference to the utilization of waste products in connection with blast furnaces have been very remarkable; and, unless I am incorrectly informed, there is not a single blast furnace extant that to-day is fully utilizing all the demonstrated improvements. Take for example one of the recent instances. It has been found that by removing the moisture from the air that is blown into a blast furnace, a very largely increased production per ton of coke in output of iron is the result. That is only one phase of the subject. The blast furnace we look upon as one of the most perfect of our metallurgical operations of to-day, and yet there is a field here to be cultivated, which indicates that there are several lines in which improved blast furnace operations can be carried on by utilizing all the waste products. Among those, especially the gas products have gone to waste most ridiculously in all parts of the world.

Mr. Herbert Dow: I read in the papers about waste blast furnace gases. I have been to the Edgar Thomson Works, and have visited blast furnaces in a number of different places, but I never saw any waste gas, as all of it was used under boilers. You may waste more power in a steam boiler and engine than you will by using the same gas in a gas engine, but other expenses are not wasted to more than offset it. If all the power plants from which we have data at present are compared, and if a liberal allowance for interest and depreciation is taken into consideration, it will clearly show the steam plants to still be the most economical. It may not be so with the improvements that may take place in the future; but as to calling blast furnace gases waste gases, I do not see why we should do so, any more than we should call coal "waste coal" when we burn the coal under a boiler. If the investment becomes too great, no amount of economy can compensate. As an example of a case of this kind, I will mention a proposed water power in our vicinity. The first cost of this plant will be so great in proportion to its output that the interest alone, when figured at only 4 per cent., will make the power cost more

than we would gladly sell the power for, in spite of the fact that we buy coal and they do not buy their water. Whether it be a gas engine plant or a dam, there is a certain investment that cannot be exceeded, or competition with steam will be impossible.

Mr. Rossi: I mean by that the surplus which could be obtained from a certain amount of gas generated in the blast furnace, if burnt under proper conditions. What you say about England is so; but in Scotland they burn raw coal, condensing the gases the same as is done when these gases are used in coke smelting. They use soft coal, they don't use coke generally. In Scotland they have apparatus for collecting the gases, and there they burn the gases for the purposes you mention; but it is not so with coke.

Mr. Henry S. Blackmore: I had occasion recently to investigate a very interesting invention, having for its object the utilization of energy which goes to waste through the furnace gases at present. The invention originally had for its object the precipitation of moisture from the air employed in cupola or blast furnaces by exposing the air during its passage to the furnace to the action of a silent electrical discharge which was supposed to cause the moisture to condense, resulting in its precipitation. However, it was found upon investigation, that while the moisture seemed to disappear, there was really no precipitated moisture that could be collected. On more careful investigation, however, it became evident that the silent discharge actually caused the combination of the nitrogen with the oxygen of the air, producing nitric oxide, a compound containing more energy than the free oxygen or nitrogen of the air as it originally passed in, and this nitric oxide being taken up by the moisture present, resulted in the formation of acid compounds volatile under ordinary conditions, which accounted for the disappearance of the moisture. The silent electrical discharge was produced by generators operated by a gas engine employing the furnace gases which ordinarily are wasted as a source of power. When we consider that the nitric oxide thus produced by the silent electrical discharge, when decomposed, evolves energy absorbed in its formation equivalent to 21,575 heat units (Thomsen), the importance of the invention becomes at once apparent, as may be readily seen by the following comparison:

$$N + O = NO = \begin{array}{l} 21{,}575 \text{ heat units absorbed (Thomsen)} \\ \text{and evolved on decomposition.} \end{array}$$

$C + O = CO = 29{,}000$ heat units evolved (Thomsen).
$NO + C = N + CO = 50{,}575$ total heat units evolved.

It can thus be seen that a large amount of energy may be indirectly returned to the furnace by utilizing the waste furnace gases to generate power to produce a silent electrical discharge which, when caused to act upon air conveyed to the furnace through the blast, results in the formation of nitric oxide with the absorption of energy which is evolved as heat energy in the combustion zone of the furnace, thus adding heat to the heat ordinarily produced by the combustion of carbon and oxygen therein.

This process is the invention of Mr. Ellery F. Coffin, and was in operation at the Muirkirk Furnace, Muirkirk, Maryland.

Mr. E. A. Sperry: While in full sympathy with all attempts to cheapen power, I would like to confirm Mr. Dow's results. I do not think the time has come yet when we should get under any great amount of excitement over cheap power from blast furnace gases. In the old country, where money is very cheap and where the interest factor can be held as low, probably, as is possible anywhere in the world, it is barely possible to skim along in competition with steam; but in this country, where our interest factors are something considerable, and have to be, and where we have cheaper fuel, the cost of power from the blast furnace operated gas engines (considering treating plant, and everything that is to be considered as entering the make-up and operating expense, makes the cost much higher than would at first seem possible. The interest factor alone in many calculations will be found to be double that of steam, and nearly as much as you can generate that same power for in other ways, and with operating expenses considerably more than you can buy it for from some of the operating water-powers that are now running.

Dr. J. W. Richards: Mr. Rossi has taken some figures from Mr. Gayley's paper, and I would advise Mr. Rossi that the figures on the bottom of page 4, using 40,000 cubic feet of blast per minute in one case and 34,000 cubic feet in another, are probably incorrect. They are correctly taken from Mr. Gayley's paper, and they represent the piston displacements in the two cases; but an exact analysis of the condition of the furnace under both those runnings (with dry blast and moist blast) has shown that the fur-

nace was receiving practically 30,000 cubic feet of air per minute, as blown in both cases, although the engine was running some 16 per cent. slower in the second case than in the first. The only plausible reason I can assign for that is that there was a higher efficiency in the pumping; but any conclusion based on those figures may be slightly erroneous.

With regard to the general subject of the utilization of gases in the gas engines, I do not sympathize with the position of Mr. Sperry and of Mr. Dow that in this country we have such very cheap fuel that we can afford to not be economical. I think that in this country we are rapidly approaching the time when we must look to the greatest economy in all our commercial operations. When I was a boy in England—not a half-century ago—I remember seeing the blast furnaces there, all with open top, lighting up the country at night for miles around like huge torches; and that was the reason why the gases were called waste gases—because they were always wasted. Now England has learned to utilize those gases; but they are still called the waste gases from the furnace because that was their original name.

Mr. Dow has spoken of the conditions being different in Europe, and that is the reason why the introduction of the gas engines in this country is slow. There are some 300,000 horsepower being utilized in Europe from the consumption of the blast furnace gases; and the only reason why we have not kept up is because of these different conditions, namely, that fuel is cheaper with us, and labor is dearer; but there is not the slightest doubt that those economies which are possible there are also possible here, and that within a very few years—possibly three or four—many of the large blast furnaces around Pittsburgh will be equipped with complete sets of gas engines such as those that are around Buffalo; and that the directors of the United States Steel Corporation (I was talking within a month with Mr. Gayley himself) are very keen after all of the economies which are to be obtained. They cannot afford to neglect them, and they are not going to neglect them; but they are going to obtain all the economies which can be obtained from the utilization of these waste gases from the furnaces, and plans and drawings have been and are being gotten up for many of the blast furnaces of the United States Steel Corporation to do this very thing.

With regard to the utilization of this energy more economically in the steel works or the iron works, here is an actual fact: Coal could be taken and used in the blast furnace for reducing the iron ore, and if all the gases which come from the furnace were utilized in gas engines to run dynamos, and the induction furnace were used for melting down the crucible steel, the steel could be melted and made with a less consumption of fuel altogether than is actually used for making crucible steel at the present time. At the present time, for a calorific power of 100, of the fuel used, the hot melted steel in the crucible contains about 3 per cent. of the calorific energy of the fuel. The following system is a distinct commercial possibility: Take the same fuel; convert it into gas; the gas will have 90 per cent. of the calorific power of the fuel. Utilize that in the gas engine. The energy delivered will be 22½ per cent. of the calorific power of the fuel, that is, 25 per cent. of the calorific power of the gas. The dynamo will give you in electric energy 20 per cent. of the calorific power of the coal; and the induction furnace will convert at least 50 per cent. of that into heat in the steel. Recent experiments with the induction furnace in America have shown an efficiency of 85 per cent. of the energy of the electric current represented as actual sensible heat in the melted steel. That was given me by a gentleman who has been working the process and whom I have known for some years, and in the reliability of whose statement I have every belief.

Therefore with a system of taking the fuel, converting it into gas and then generating the electric energy and melting the steel, an efficiency of over five times that which was obtainable from melting with fuel—using the fuel direct—is directly possible. There is a large field, then, in connection directly with the blast furnace for converting the product of the blast furnace into fine qualities of steel (I do not speak of the ordinary qualities); and in doing so, the use of energy which will be obtained from the blast furnace by means of the utilization of the gases is going to play a very large part.

I do not believe that within the next decade there will be any application of this electrical energy to the common grades of steel. The Bessemer converter and the open-hearth furnace are too cheap for that; but for the finer qualities of steel there is no

doubt in my mind that the manufacture of crucible steel in crucibles is an industry which is doomed within the next five years, and that the chief factor in the electrical manufacture of the fine qualities of steel will be the power obtained from the waste gases of the blast furnace.

Mr. Dow: In our locality we expect to get power from a dam for nothing, in connection with municipal work, so that they only have to pay about 4 per cent. for the money that they invest in that dam. Taking the amount of power that is being derived from that dam, figuring that they are getting practically all the power that there is in the water to-day, we would be glad to furnish them the power that they will get for that 4 per cent.; that is, we would be very glad to furnish the total amount of power they will get from that dam for what would be interest on their bonds, to say nothing of the other expenses that they involve. Now they are burning coal, or we are burning coal, very wastefully; looking at our great-grandchildren we are probably very prodigal of our coal; but as a strictly business proposition in the light of the present time, we would be very prodigal of our dollars and cents if we did not burn it that way.

Mr. W. McA. Johnson: I would like to ask what the price of that coal is? I suppose it is slack coal.

Mr. Dow: It is $1.50 for slack coal.

Mr. Rossi: In Pittsburgh at the furnace the price of Connellsville coke is $2.50 to $2.60 a ton.

Mr. Dow: No, I beg to differ with you; you can get coal in Pittsburgh with 14,000 B. T. U. in it for less money than we are paying for coal with 11,700 B. T. U. The regular price for run of mine coal around Pittsburgh is less than $1.60.

A paper read at the Seventh General Meeting of the American Electrochemical Society, held at Boston, Mass., April 27, 1905. President Carhart in the chair.

THE ELECTROSTATIC TREATMENT OF ORE.

By Lucien I. Blake.

If a small portion of a substance be brought into contact with a charged body, it will tend to acquire the potential of that body. This will be accomplished, if at all, by the imparting of electricity to the small particle. The charge will diffuse itself over the surface and through the substance until finally it will reside wholly upon the surface.

This process may be practically instantaneous or it may take an appreciable time. During the time, however, the particle is subjected to the inductive influence of the charge and is, therefore, bodily attracted. Further, during the acquiring of the charge, this attraction is being offset by an increasing bodily repulsion which finally prevails to repel the particle. Thus every kind of particle is eventually hurled from a charged surface. What is true of a single particle is true in general of a mass of particles, but the time of acquiring an individual charge is greatly modified by the mass.

Each particle has a specific time-element for acquiring a given potential. If V be the potential of the charged surface, the time for a particle to acquire the potential is:

$$t = R\ C \int_0^Q \frac{dQ}{Vc - Q} = -.4343\ R\ C\ \log_{10} \frac{Vc - Q}{Vc}$$

where C is the electrical capacity of the particle in its position of contact, Q its charge at any instant, and R its electrical resistance. This is easily obtained from the differential equation for the energy supplied to a circuit containing resistance and capacity without inductance, namely $Vi\ dt = Ri^2\ dt + \frac{Q}{c}\ dQ$.

Since Q is evidently very small, the $\log \frac{(vc - Q)}{vc}$ is always exceedingly small, and the value of t will depend upon the other two factors, R and C.

Of these factors the resistance, or its reciprocal, its conductivity, is made up of the resistance of the material of the particle, together with the resistance at the surface of contact of the particle with the charged surface. This latter may be very great.

Of these factors, the capacity of the particle depends not only upon the size, shape and position of the particle itself, but also, in an exceedingly interesting way, upon the number, relative proportion, character and arrangement of neighboring particles. This capacity factor, C, I am led by experiment and commercial experience to believe plays an important role in the successful electrostatic separation of ores. Evidently, then, the time element which thus controls the duration of adherence of particles to a charged surface depends, for a given potential, upon both conductivity and capacity.

This dependence will be taken up somewhat in detail later. If these conceptions of conductivity and capacity be applied to a mass of crushed ore, it is clear that each particle may be considered to have its special time element during which it clings in the charged surface and at the end of which it is repelled. The time range is practically from instantaneousness in good conductors to many days in good insulators, with all intervals between.

This time element, which is characteristic of the different materials in ore, has been first recognized and applied by Mr. L. N. Morscher, graduate student of the University of Kansas, together with the writer, as the basis of a practical method for the electrostatic sorting of ore. The commercial development of the machine has been largely due to Mr. W. G. Swart, mining engineer, of Denver.

The elementary steps in the method are naturally four: First, the crushing of the ore to a fineness sufficient to break apart the crystals; second, the drying of the ore; third, the suitable feeding of the ore to a charged surface; fourth, the collection and removal of the separated products.

The simplest form of the device involves the delivery of the ore in a thin sheet to an inclined and charged metallic surface, and then suitably collecting the repelled particles. The material of slow charging will slide gradually down the plate and be repelled at different points.

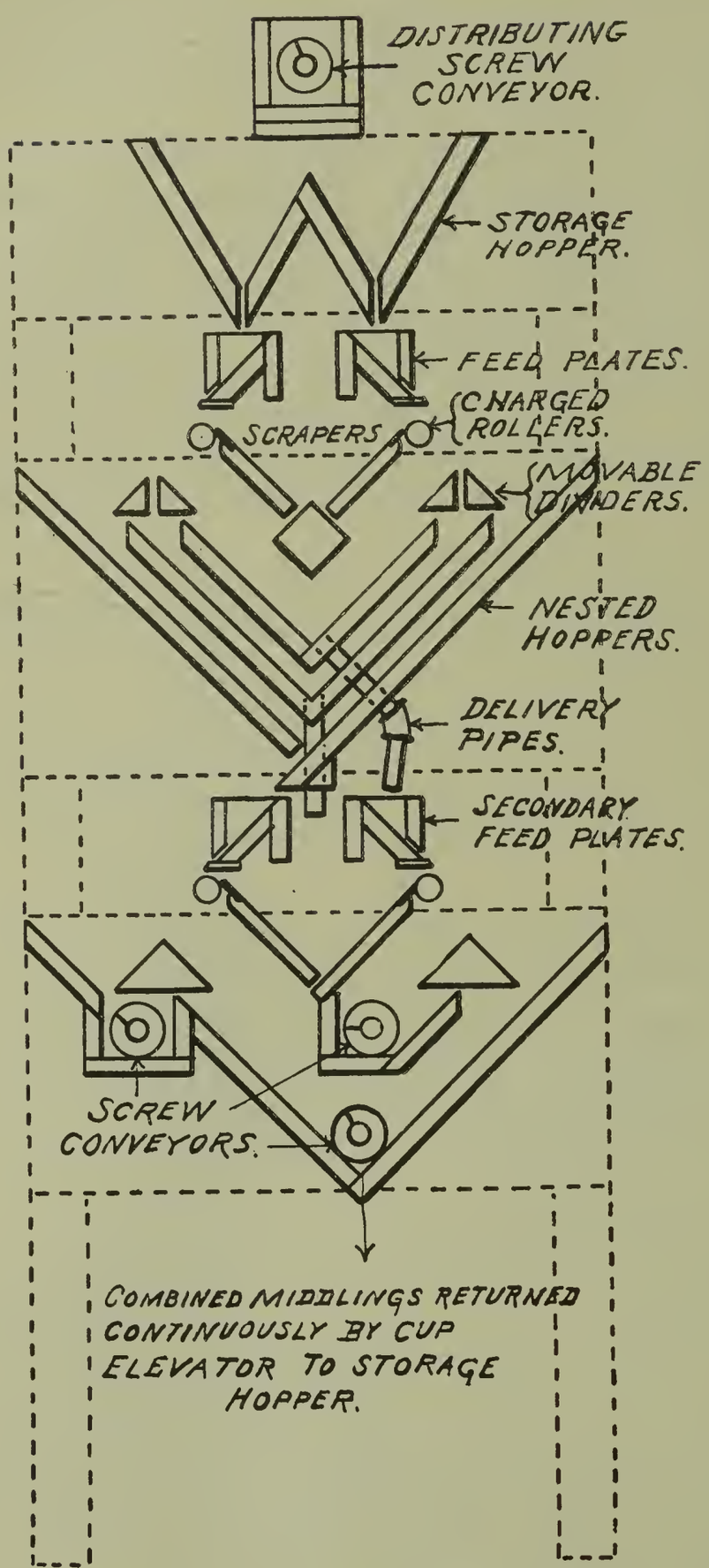
A second simple device is a horizontal slowly revolving charged metallic roller, with ore delivered in a thin sheet along its surface, and with bins arranged at selected places to collect and to deliver separated products. Both of these devices are in commercial form and use to-day.

While there exists naturally a specific conductivity for the different minerals, this may not be the same for any given mineral from different localities. The presence of impurities, surface changes by oxidation, etc., may alter the conductivity. It is possible, however, to arrange the minerals roughly into two general classes, which may be called A, conductors, and B, non-conductors. The following list has been made out by W. G. Swart, mining engineer, from his practical experience, both in the laboratory at Denver and from various commercial plants which he has supervised:

A—Conductors.	*B—Non-Conductors.*
Native Metals	Quartz
Pyrite	Calcite
Chalcopyrite	Limestone
Galena	Porphyries
Graphite	Slates
Molybdenite	Sandstones
Copper Glance	Garnet
Silver Glance	Spinel
Gray Copper	Zinc Blende
Most Sulphides	Lime Carbonate
Most Copper Minerals	Barite
Most Iron Minerals	Gypsum
Most Silver Minerals	Granite
Most Manganese Minerals	Fluorspar
Tellurides	Most Silicates
Black Sands	Most Gangue Rock.

In the majority of cases it is commercially sufficient to separate the ore into two products, which represent these two classes. Occasionally, however, two conductive minerals may be separated from each other where there is practically a marked difference in their time elements.

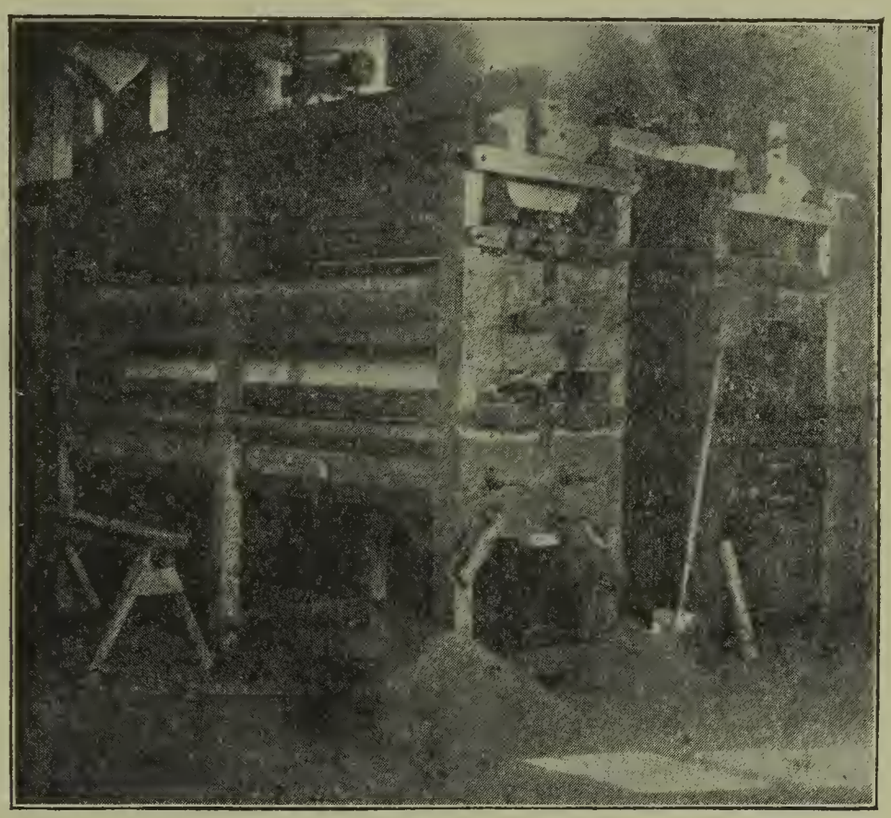
Among the non-conductors this time difference is ordinarily


DISTRIBUTING SCREW CONVEYOR.
STORAGE HOPPER.
FEED PLATES.
CHARGED ROLLERS.
SCRAPERS
MOVABLE DIVIDERS.
NESTED HOPPERS.
DELIVERY PIPES.
SECONDARY FEED PLATES.
SCREW CONVEYORS.
COMBINED MIDDLINGS RETURNED CONTINUOUSLY BY CUP ELEVATOR TO STORAGE HOPPER.

sufficient to make a commercial separation, as, for example, zinc blende from quartz, garnet or heavy spar.

To take advantage of the different conductivity and capacity of ore mixtures, as mentioned above, the general plan of the machine is as shown in the accompanying diagrammatic sketch, in which there are four drums.

A general view from a photograph of a Standard machine in operation is also given:



The machine is built chiefly of wood in two sections, which may be set tandem or abreast, the dimensions being 12 x 12 x 7 feet high; weight about 5,000 pounds.

The two top drums work on the material first fed into the machine. By these the ore is separated into two general classes: the one containing a large majority of conductors, the other of non-conductors. Each of these products is then re-treated on a lower drum. The potential of the upper drums is usually alike, but each of the lower drums is adjusted according to the particular ore. A middlings product is taken from the lower drums and re-fed to the upper hoppers. The whole process is continuous and automatic. Thus, it is seen, a first separation is made

into two general products, differing greatly in conductivity. Then each of these products is further separated by changing the voltage of the repelling surface, altering the feed, speed of drum, etc., these successive steps being carried out in the same machine.

By suitably controlling these steps, four drums, in general, suffice to give the greatest capacity and to keep the process continuous and to deliver finished products suitable for smelting.

It is in these successive steps, after the first separation, that the electrical capacity of the ore particles, as alluded to above, plays it role. It is within our commercial experience to control, at least to a sufficient extent, the time element of the metal content of most ores by controlling the electrical capacity of the ore ingredients, subsequent to the first separation.

This is technically called "balancing." It is done by changing the capacity factor in the time equation. This control is obtained by properly proportioning the first two separation products for their feed to the lower drums, and then, by the use of adjustable dividers, change of feed, etc., it is possible to one skilled in the art to divert into one general direction these particles, which are thus made to have practically the same time element.

This is done by the operator without interruption of the machine.

Further, the fact that the conductivity of the particles depends chiefly upon the nature of the *surface* of the particles has led us to methods of artificially altering the surfaces. Already Mr. Swart has developed over 200 treatments whereby, by chemical, thermal and other means, it is possible to alter the time element of one or more of the ingredients of ore and make them amenable to electrostatic separation.

The source of electricity for this process can be any static generator. The voltage sufficient at the generator is about 350,000 volts. This voltage is being successfully carried from any central generator room to machines situated in any part of a mill.

From the constant potential mains each machines receives the full voltage, which is then adjustable by a simple device to any range which is different for the different drums. Through three years now of experience in the dampness, dust and dirt of the usual concentrating mill, I think it is proven that the transmission

and use of static electricity is commercially and economically feasible. We have now about 40 Wagner micaplate static generators running 24 hours each day, under care of the usual help of concentrating mills. At the high voltage used the leakage at the machine is considerable, but, including it, the electric power

Description	Products	Per Cent. Zinc	Per Cent. Lead	Per Cent. Iron	Remarks
LEADVILLE, COLO.	Orig.	30.48	3.21	21.60	20 Mesh.
Zinc Middlings.	Iron	9.04	8.00	35.11	Combined. Iron
Wilfley Tables.	Zinc	51.20	0.62	6.40	4.87 %
JOPLIN, MO.	Orig.	49.53	2.52	10.78	10 Mesh.
Zinc Middlings	Iron	2.92	9.92	34.44	Lead practically
from jigs.	Zinc	61.31	Trace.	1.57	all removed.
BENTON, WIS.	Orig.	29.15	5.16	10.90	6 Mesh.
Zinc Middlings	Iron	5.07	8.40	38.88	Sold to acid
from jigs.	Zinc	58.44	0.23	1.16	burners.
SILVERTON, COLO.	Orig.	23.12	8.00	23.87	
Zinc Middlings.	Iron	9.04	15.56	30.35	24 Mesh.
Wilfley Tables.	Zinc	49.73	2.08	4.77	
IDAHO.	Orig.	25.87	20.40	12.02	
Lead and Zinc	Lead	4.45	50.58	16.14	High Silver.
Table Concentrates.	Zinc	45.11	3.81	7.40	
		Copper.			12 Mesh.
NEVADA.	Orig.	3 20			Saving 81% of the
Chalcopyrite in	Conc.	12.94			Cop'r. Crude Ore.
Garnet.	Tlgs.	0 40			No dust removed.
ARIZONA.		4.60			20 Mesh.
Copper Carbonate	Orig.	33 89			Saving 70% of the
in Limestone.		0 79			Cop'r. Crude Ore.
					Heated to redness.
MICHIGAN.	Orig.	2.68			30 Mesh.
Native Copper in	Conc.	38.70			Saving 76% of
Sandstone.	Tlgs.	0.27			Copper.
UTAH.	Orig.	6.06			
Chalcopyrite in	Conc.	26.81			Saving 88%
heavy Spar.	Tlgs.	0.93			Copper.
			Iron.	Oz. Gold.	
NEW MEXICO.	Orig.	1.14	11.60	0.80	Saving 74% of the
Gold-bearing Pyrite	Conc.	4.20	36.12	2.42	Gold.
in Quartz.	Tlgs.	0.33	1.27	0.14	

per standard machine of 15-ton 24-hour capacity is only about ¼ horse power, the total expended per machine being only about 1 H. P. The generators are run in battery.

Many thousand different ore samples from all parts of the world have been tested in the laboratory at Denver, in my laboratory at

the University of Kansas and in the sampling mill of Henry E. Wood in Denver, where test machines are in operation, and the results of separations, treatment and many interesting experimental facts are recorded. It may be interesting to give a few of the results being obtained each day commercially:

RESULTS.

In each case the assay of the original material as fed to the machine is given first, followed by the assays of the products made by the separator.

Some lots also contained considerable gold and silver values, which largely follow the lead and iron.

Commercial work has also been done, separating molybdenite from gangue, the resulting concentrates containing 96 per cent. pure molybdenite.

Graphite has been commercially cleaned from silica and feldspar.

Hornblende has been separated from apatite.

Ilmenite has been separated from rutile and from phosphate rock.

From a scientific standpoint, the action of the individual ore particles, under the influence of electrostatic stress, due both to direct and induced charges, the effects of conductivity and capacity of the particles, the presence of air currents and leakage points within the machines, the question of proper voltage, of mechanical feed of highly charged particles, of mutual electrostatic repulsions, have all led to many new problems in applied electrostatics, many of which for commercial reasons are not even alluded to in this paper.

School of Engineering,
University of Kansas.

DISCUSSION.

President Carhart: This paper of Professor Blake is open for remarks.

Mr. C. P. Townsend: I notice it stated that the middlings are

returned and finally disappear. Did I understand that these are middlings because they are intermediate in conductivity?

MR. LOCKE: Yes.

MR. TOWNSEND: I do not just see why they should disappear, or why they should pass on returning either into the conductors or non-conductors.

MR. LOCKE: By arranging the divider you can finally split those middlings by the eye, so that you will throw the richer part of the middlings into the concentrates and the poorer part into the tailings. It is simply a commercial division.

MR. TOWNSEND: It amounts simply to a closer first division.

MR. LOCKE: Yes. Commercially four machines may be placed in series. The stream of ore to be treated is carried over the four machines, and a part (approximately one-fourth) is deflected to each machine. The middlings from the first machine are elevated to join the main stream of ore going to the second machine, and so on. The middlings from the fourth machine may be returned to the same machine.

PRESIDENT CARHART: Anything further?

MR. CARL HERING: I notice in that diagram the non-conducting particles are shown as adhering to the roller. Do they actually stick to the roller, or simply are not repelled?

MR. LOCKE: They simply slide off. For a pure non-conductor there is no repulsion, and it is acted on only by the force of gravity.

DR. J. W. RICHARDS: I would ask whether those very difficult materials, the Broken Hill sulphides, have been tested on this machine, and, if so, what were the results?

MR. LOCKE: I have to say that I am unable to answer that question. Professor Blake was unable to be present, which I very much regret. I think the Broken Hill materials may have been treated because they have tested almost everything in the line of zinc products.

DR. RICHARDS: It is the material from Australia which occurs there in such enormous quantities, and is at present thrown on the dump.

MR. LOCKE: They are working this Broken Hill material by the sulphate process.

A paper read at the Seventh General Meeting of the American Electrochemical Society, held at Boston, Mass., April 27, 1905. President Carhart in the chair.

EXPERIMENTS WITH THE REDUCTION OF DIFFERENT OXIDES OF LEAD BY ELECTRIC CURRENT.

By A. Lodyguine.

About three years ago, when I was connected with the National Battery Co., of Buffalo, which manufactures the storage batteries of Mr. E. A. Sperry, the question was raised as to the possibility of electrically extracting lead from the peroxide of lead of old storage batteries, instead of selling this peroxide to the junk dealers.

A series of reasonings, which it would be too long, and probably not necessary, to enumerate here, brought me to the com-

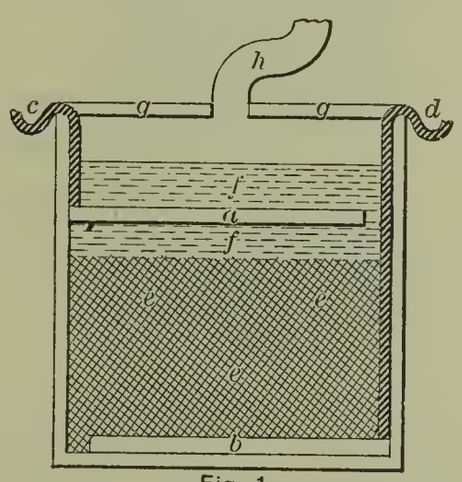


Fig. 1

position of the following mixture as most adaptable for the purpose:

Peroxide of lead, PbP^2	200	grs.
Chloride of sodium, NaCl	100	"
Sulphuric acid monohydr., H^2SO^4	131,5	" Solution of
Water, H^2O	168,5-2	" H^2SO^4 at 30 % B.

A glass jar, with lead electrodes, was prepared to receive the mixture.

In Fig. I, *a* is the negative electrode; *b* is the positive electrode; *c* and *d* are the insulated conductors connecting the electrodes

with the battery giving the current; *e* is the above-mentioned mixture, and *f* is some of the liquid part of that mixture; *g* is a cover, with a pipe, *h*, by which the gas escapes.

When the mixture was introduced into the jar, the liquid part poured on, and the whole mixed with a glass stirrer, the chlorine gas began to escape by pipe *h*.

The setting free of chlorine soon stopped, because hydrochloric acid could not continue to be replaced by sulphuric acid in the chloride of sodium without the application of heat or of electric current.

The instant that current passed through the mixture a violent setting free of chlorine occurred, and there appeared a formation of chloride of lead in the solid mixture.

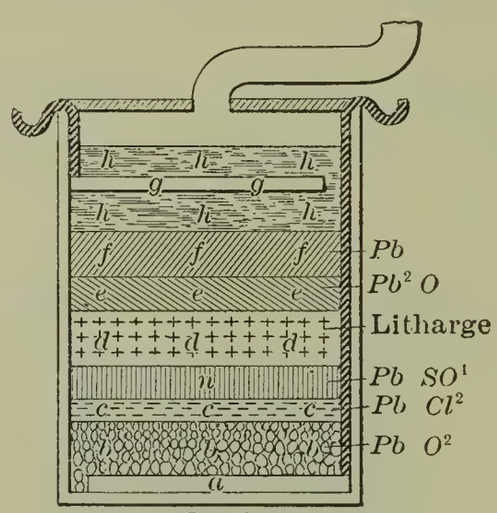


Fig. 2

After a certain time, the length of which depended on the density of the current, a formation of some sulphate of lead was noticed.

After another period of time some litharge was formed; finally, at a certain stage of the process, the mixture in the jar presented the appearance shown in Fig. II.

a is positive electrode; *b*-PbO^2; *c*-$PbCl^2$; *d*-Litharge; *n*-$PbSO^4$; *e*-Suboxide of lead, Pb^2O; *f*-spongeous lead; *g*-negative electrode; *h*-liquid part of mixture.

The distinctness and neatness of the appearance of these strata were extremely spectacular and interesting. To the end of the experiment, one could follow the increase and decrease of the different strata and their transformation into one another. At

last only spongeous lead remained in the jar, all of the mixture having been transformed into it.

To establish the commercial value of the process, I made a series of these experiments, using different densities of current.

The surface of each electrode was one square decimeter.

The following table gives the numerical results of my experiments:

A	V	W	grs.	hours	grs. per AH.	grs. per WH.
10	4.35	43.5	172.5	11.5	1.5	.345
8	3.85	30.8	138	11	1.50	.378
6	3.20	19.2	138	14	1.64	.514
5	3.00	15.0	138	16	1.73	.575
4	2.70	10.8	138	18.5	1.87	.691
3	2.40	7.25	69	11.5	2.00	.833
2	2.07	4.14	69	15.5	2.25	1.075
1	1.71	1.71	46	18.5	2.50	1.454
.5	1.55	.775	46	33.5	2.75	1.77
.2	1.45	.290	23	38	3.00	2.10

A is the density of the current per square decimeter; *V*-volts; *W*-watts; *grs.*-weight in grammes of all lead decomposed during the experiment.

hours is the duration in hours of the experiment.

grs. per { *AH.*-ampère hours. *WH.*-watt hours.

As we see, with a density of current equal to .2 ampères per square decimeter, the amount of lead deposed per watt hour is equal to 2.1 grammes, and per ampère hour it is 3 grammes.

The electrochemical equivalent of lead is 3.8581 grammes per ampère hour.

At the rate of 2.1 grammes per watt, about 435 KWH. are needed for the extraction of one short ton of pure lead from peroxide of lead. At a price of current of $15 per KW. year, the cost of the above current for the extraction of one short ton of pure lead is about 87 cents.

It is evident that the cost of the current may be a great deal higher before it becomes too expensive for this purpose.

A paper read at the Seventh General Meeting of the American Electrochemical Society, held at Boston, Mass., April 27, 1905. President Carhart in the chair.

COLLOIDS.

By W. R. Whitney.

The purpose of this paper is to call attention to the analogies which a study of colloids has thus far brought to light in several apparently remote fields. Some such fields are the production of all precipitates in solutions, the chemistry of proteids, blood immunity and infection, dyeing of textile fabrics, the coloring of glass, the settling of slimes, the cementing of clays, electrical endosmose, etc.

We, as electrochemists, are concerned with this subject because, in the colloidal state, material acts as though it consisted of staticly charged particles. It is coagulated or precipitated by electrolytes and undergoes migration with the electric current, closely imitating the migration of electrolytic ions. To show this experimentally we apply the direct current of 220 volts to two tubes, containing in one case a colloidal solution of ferric hydrate and in the other colloidal arsenic sulphide. These are U-shaped tubes, having their tops covered with gold-beaters' skin membrane, to prevent convection, and outer tubes surrounding the separate arms of the U tubes which contain distilled water and platinum electrodes. It will soon be apparent that the arsenic sulphide moves away from the cathode membrane, while the ferric hydrate moves away from the anode membrane.

There is a state of matter in apparently homogeneous distribution throughout a liquid to which we give the name suspension, or emulsion. As the degree of fineness of matter suspended in a liquid is increased a state is reached where no settling or separation into layers occurs, and yet the properties of the mixture are not entirely those of a homogeneous solution. The difference between a fine state of permanent suspension and one of real solution may not be one of kind, but there are at least qualitative differences which require the distinction. In this paper we are dealing with that class of mixtures in which the suspension is

permanent and the general criteria of solutions are not met by the mixture. In collecting the various possible representatives of this condition for the purpose of seeking analogies, we are in danger of overdoing the work, but it is instructive to proceed in this way and to test the propriety of the classification in each case. We may distinguish between suspension and solution by confining the latter term to homogeneous mixtures capable of exhibiting definite osmotic phenomena. We then retain, at least temporarily, all other mixtures under the title of suspensions. It is probably true that a gradual state of transition exists between the two forms of matter, so that a sharp line of demarcation cannot be drawn. Sugar dissolves in water, and is a clear case of simple solution. Salt also dissolves and results in a somewhat different kind of solution, one in which the osmotic phenomena are nearly twice as marked as in the case of sugar. Gelatine apparently dissolves in water, but osmotic phenomena of the solution are almost, if not quite, absent, and the solution might be called a suspension. Ferric hydrate, silicic acid, and in fact many insoluble substances, may be made to assume a state of apparent solution in a liquid, but in all such cases there is also a noticeable absence of measurable osmotic phenomena.

All finely comminuted insoluble material in suspension exhibits certain properties characteristic of a state intermediate between evident solutions and visible and temporary suspensions. We may also include in the group of suspensions a multitude of biological liquids, such as blood, with its suspended corpuscles, blood sera, with their many and varying organic antitoxins, antiferments, cytotoxins, agglutinins, precipitins, etc., sera, with their ferments, etc. Professor Noyes has suggested the terms "colloidal suspension" and "colloidal solution" as a means of dividing the field into two parts. This is often of benefit, but for the present we do not wish to thus distinguish them. It is certainly simple to recognize in colloidal platinum a distinct state of suspension which it is impossible, except with the purest water or some special admixture, to keep from rapid coagulation or deposition. It is also simple to recognize in an aqueous solution of gelatin a permanent state so closely allied to real solution that it cannot be surely distinguished from it. But between these two extremes there is an endless number of mixtures which have the common

and peculiar properties of colloids. Some of these peculiar properties are the following:

1. As already pointed out, they all appear to be solutions, but they display little or no osmotic phenomena.

2. They possess no saturation point or limit of solubility or miscibility. A supersaturated state is impossible with them, and so also contact of solid with the solution will not cause deposition, as it does in the case of supersaturated crystalloids.

3. In some cases, at least, they exert marked effects on one another, imitating to perfection the chemical reactions of crystalloids. Some precipitate others, while some render others more difficultly precipitable by electrolytes. As shown by experiment, the arsenic sulphide which migrates as a negatively charged body will unite with ferric hydrate, which migrates as a positive body, and forms a precipitate containing both substances.

4. They are precipitated, usually, by very small quantities of electrolytes, and there are remarkable rules in this case which are based on what is called the electric charge of the ions of the electrolyte.

5. So far as microscopic powers go, many colloids have been seen to consist of distinct particles in suspension, and in most cases the size of these particles is about at the limit of the microscopic vision—that is, they are of the general order of magnitude of the wave length of light. In all cases these particles are in a very irregular and peculiar motion, first described by Brown, and called the Brownian movement. This motion reminds one of nothing else so much as of the hypothetical kinetic motion of molecules.

6. A beam of light passing through these heterogeneous mixtures often appears like a beam through a dusty atmosphere, and the ray is polarized by the mixture.

7. Under the influence of the electromotive force between electrodes in the colloidal mixture, the suspended matter migrates toward one or the other electrode. This is also a property of solutions of electrolytes, but in the case of colloids the current carried by the migration of the material is almost if not immeasurably small. All colloids have a very low rate of diffusion, and there is no scheme of filtration which is at all satisfactory in

separating them from simple solutions. Many of them pass readily through unglazed porcelain.

Methods of producing colloidal mixtures will now be considered.

All of our work on the subject has led to the conclusion that whenever any substance which is by nature insoluble in a liquid is produced in a fine state of divison in that liquid, it will remain in colloidal state until coagulated or precipitated by external means. It is simply the study of possible applications to this rule that leads to the widely different experimental methods of producing the colloidal state. If a substance is vaporized into an excess of a liquid in which it is insoluble, the colloidal state commonly results. This is well shown in the case of arcing of such metals as gold, silver, platinum, mercury, etc., under water, and also by the condensation of mixed vapors, such as steam and insoluble oils in which a fine state of emulsion is produced. An arc between platinum electrodes under water, through which a current of 8 ampères was passed, produced a black solution of colloidal platinum.

This method is only slightly different from the introduction of the insoluble body in the form of a solution, as, for example, the addition of an alcoholic solution of a gum to water. In this case the gum, being insoluble in the water, assumes an exceedingly fine, perhaps molecular state of subdivision. An alcoholic solution of gum mastic added to water produced a white colloidal suspension.

Colloidal mixtures may be obtained by the direct addition of the insoluble substance in a finely divided state to the liquid in question. This is more successful the finer the state of subdivision, and will not succeed if electrolytes are present in appreciable quantities. Thus, finely divided mineral matter, such as quartz, inactive metals, which, since their reduction to metallic state have not been melted together, act in this way. Zirconium, made by the reduction of the oxide by metallic sodium, or silver, made in the wet way by reduction, pass directly into the colloidal state on being placed in water. In this same way many of the organic and inorganic dyes produce colloidal solution. Methyl blue and Prussian blue are members of these classes.

Besides adding the insoluble substance, as such, to the liquid, it may evidently be made within the liquid. Any chemical reaction

which produces such an insoluble substance without involving the use or production of appreciable concentrations of electrolytes, is quite sure to yield a colloidal state. There are multitudes of illustrations of this process. The following are a few:

$HgCy_2$	+	H_2S solutions.
As_2O_3	+	H_2S "
SO_2	+	H_2S "
$AuCl_3$	+	Phos. (or other reducing agent).
$Si(CH_3)_4$	+	H_2O

An examination of these reactions will show that in no case is there presence of even a moderately strong electrolyte. Such would cause the precipitation of the "insoluble" substance which is actually formed.

A slightly different method depends on the removal of electrolytes which form one or more factors of the equilibrium condition in which an insoluble substance is being formed. This removal may often be effected by dialysis or by evaporation, and the colloidal state then results. This is well illustrated by such cases as colloidal ferric hydrate, which may be made by the dialysis of any soluble ferric salt and the silicic acid which is made by dialysis of a soluble silicate. In this case, the acid and alkali respectively, which are due to the hydrolysis, are gradually removed and the residual insoluble product is left in the colloidal state. It is natural to expect that in the organic world many such colloidal mixtures exist. There are many plant and animal fluids in which the natural concentration of electrolytes is very low. Here we actually find countless mixtures which seem to have the properties characteristic of artificial or inorganic colloids. They are all of them cases in which the "insoluble" substances are mixed or dissolved in water, and are evidently introduced into the water a particle or molecule at a time.

It will be recognized that the blood and other sera are very complex cases in which several or many insoluble substances exist in a colloidal state. Here the corpuscles are obviously suspended, but there appear also to be many other organic materials in these fluids which must also be classed as colloids. Many of them precipitate one another, just as a positive colloid precipitates a negative one, and in this case both seem to enter into some kind of a precipitated union which consumes relatively large or equiva-

lent quantities of each. This is true in the reaction between toxins and antitoxins, ferric hydrate and arsenic sulphide, etc. The migration experiment shows arsenic sulphide to be a negative colloid, as it moves toward the positive electrode, while ferric hydrate is similarly shown to be a positive colloid. All colloids migrate in one or the other direction.

It seems to be a general rule also that a positive colloid will coagulate a negative one, while those of the same sign apparently have no effect on one another. Thus the positive, ferric hydrate, coagulates the negative, arsenic sulphide, while Prussian blue and other negative colloids do not.

In the case of blood the serum of one animal will usually precipitate the corpuscles from the blood of another. For example, a rabbit's blood is precipitated by the blood serum of a chicken. The serum of one animal species being injected into an animal of different species gradually produces in the blood of the latter a so-called precipitin. If, now, some of this diluted and clear blood-serum be treated with the clear serum of the former animal a precipitate will be produced which would not have been produced by a mixture of the original sera. The animal treated with the foreign serum was immunized to the specific serum employed. In the case of these precipitations there are several peculiarities which are also observed with inorganic colloids. For example, a low concentration of electrolyte, or other precipitating agent, introduced into the colloidal mixture, whether it be artificial or natural, organic or inorganic, or a simple suspension of bacteria, produces no visible effect. A higher concentration produces a precipitate, which precipitation, up to certain concentrations, takes place the more rapidly the more concentrated the precipitant used and the more concentrated the colloidal mixture.

Blood serum may be also made to produce specific organic compounds, so-called agglutinins, which cause the coagulation of disease germs and bacteria, and this coagulation takes place whether the germs and bacteria are living or not. This agglutination of bacteria is used in many cases as a method of recognition of specific bacteria and of diseases, for it has been found that while the serum of an immune to a disease may precipitate the germs or bacteria of some other kindred diseases, it is markedly most powerful in its action in precipitating the bacteria or germs of the specific disease in question.

In most cases, at least, it has been shown that the presence of traces of salts is necessary in this precipitation of bacteria and germs. Joss found that anti-typhoid serum does not agglutinize the typhus bacilli in the absence of salts, and Bordet had earlier found that washed cholera germs could be agglutinated from saline solutions, but not from pure water, by its specific anti-serum. There are many interesting and important cases in nature where this phenomenon, involving the presence of traces of salts, is concerned in the coagulation of growing plant and animal material.

One of the most marked properties of the inorganic colloids is the ease with which they are precipitated by electrolytes and the laws governing this precipitation. Briefly, all those which migrate with the negative current are precipitated by very small amounts of positive ions, while the positive colloids are coagulated by negative ions. This has been quite extensively experimented upon, and the following table shows the results in the case of certain concentrations of arsenic sulphide and ferric hydrate, as measured by Freundlich:

	ARSENIOUS SULPHIDE	FERRIC HYDRATE
	Negative	*Positive*
Salt	Conc. millimol per litre	Conc. millimol per litre
KCl	69.	9.0
KNO_3	69.8	11.9
KI	67.	16.2
$NaCl$, etc.	71.	9 2
K_2SO_4	91.5	0.204
$\frac{BaCl_3}{2}$	1.	9.6
$MgSO_4$, etc.	1.13	0.217
$AlCl_3$	0.13	
$CrCl_3$	0.13	
$FeCl_3$, etc.	0.13	

The following are some of the other well-known colloids:

Positive	*Negative*
Certain dyes	Certain dyes
Metal hydrates	Silica
(Se, Th, Al, Cr, Fe)	Sulphides
Asbestos	Metals

From the data it will be seen that the valance, or better, the electric charge of the active ion, is also of great importance in determining the concentration necessary for precipitation. All potassium salts have about the same quantitative effect in precipitating the negative arsenic sulphide, and this is about 60 times less marked than the precipitating power of the divalent elements, such as calcium, and is about 500 times less marked than the trivalent elements, such as aluminum and iron. The nature of the negative ion scarcely influences the result. On the other hand, with the positive ferric hydrate, it is seen that the reverse is true. The negative ion is the determining factor and the power of precipitation varies widely with the valance, being the greatest with the ions of highest valance. The effects, due to difference in valance, are seen to be exceedingly well marked.

In dyeing of textile fabrics several applications of these principles are evident. A collection of the literature on the mordanting power of various positive ions on dyes has shown that, just as in the coagulation of the colloids, so also in the setting of the dye, the higher the valance of the element the greater is its power as a mordant. Monovalent elements act slightly as mordants. Some divalent ones are even practically useful for the purpose, but iron, chromium and aluminum, the trivalent elements, are much stronger in this respect, and the few tetravalent elements tried are still more active.

Again, since colloids have only very little if any osmotic pressure, they diffuse slowly, if at all, so that wherever convection currents are absent the colloid should be stationary. This may be one reason for the lack of motion of a colloid in solid jellies, although the size of the particles may explain it as well. This fact is an observed one and gives us a particular method by which fast dyes may be introduced into the mass of a solid organic

material permeable to water, such as are, in general, the textile materials. A single example will well illustrate this point:

Ferric chloride and potassium ferro-cyanide solutions produce Prussian blue on mixing, and this is a colloid whose precipitation may be prevented by removal of the electrolytes which are formed by the reaction, if the solution is not too strong. This removal may be easily brought about by dialysis. This collodial Prussian blue will not dye or color a mass of agar jelly suspended in it, nor will it dye cotton. It shows no tendency to penetrate either of these materials. If, however, it were produced within the jelly or the cotton by the chemical reaction, it ought not to be possible to wash it out. This is shown in the case of the jelly by the sample shown which was treated, first with ferric chloride, and after rinsing, treated with potassium ferro-cyanide solution. The resulting collodial dye cannot now be washed out from the jelly, as it will not diffuse in this material. The jelly may be looked upon as a highly magnified fibre of textile material.

It seems probable that the migration of water through a porous membrane, when this is submerged between and separates two electrodes, is due to the same cause as the migration of suspended matter with the electric current. If the suspended matter were fixed in place it would seem as though the water must move in the opposite direction to that previously taken by the movable colloid. This is at least usually true. Suspended clay migrates with the negative current. A clay membrane causes the water to migrate with the positive current, as shown by experiment. Suspended asbestos migrates with the positive current, as shown by Dr. Blake, and in accord therewith the water migrates through an asbestos membrane with the negative current, as shown by experiment.

Research Laboratory, General Electric Co.

DISCUSSION.

President Carhart: This very interesting paper of Dr. Whitney is open for discussion, or questions.

Prof. Franklin: I would like to ask whether you can

detect a diminution of the concentration of the positive ions in a solution when it is the positive ions which cause the coagulation.

Dr. Whitney: Yes. Mr. Ober, of the Massachusetts Institute of Technology, performed experiments on that particular point. In the case of the negative arsenious sulphide there is a certain small quantity of the positive ion of the salt used which is carried down in the precipitate, probably as hydrate, *the supernatant liquid becoming also thereby correspondingly acid.* (See J. Am. Soc. 23. 842.)

Dr. J. W. Richards: If some exact values were obtained for the activities of these positive and negative ions, could they not be used for determining the unknown valence of ions in solution? We had yesterday a paper on the precipitation of chromium, in which there was considerable doubt expressed as to what the valence of chromium in the solution was. Those solutions might possibly have been tested in this manner in order to determine the valence of the positive and negative ions in them.

Dr. Whitney: Owing to the presence of several different positive and negative ions in most such cases, this process, which in the simple case will operate all right, will of necessity be too complicated. It is thus too complex in the case of the chromium salt.

Dr. H. R. Carveth: Have there not been many cases where the colloid in solution has been precipitated by the addition of organic solvents?

Dr. Whitney: I said nothing about this, because you see right away that if you add, say, alcohol to an aqueous solution or suspension, you change the nature of the solvent, and the solubility of that substance in alcohol might be greater or less than in the mixture. It is a very complicated case. It is perfectly possible to have a colloid suspended in a mixture of solvents, so to speak; but it is also possible to have a colloid suspended in a water and add to it a second liquid which makes a pure solution of the suspended solid.

Dr. Carveth: There is then a combined effect—part due to the undissociated body and part to the nature of the ions; and that is the reason the question was asked. As we listened to the lecture, it appeared at the time as if it were the ions alone which produced the results, whereas in all cases what we have observed must be ascribed to the combined effect of the undissociated and the dissociated parts.

Dr. Whitney: I always consider the colloidal matter as insoluble matter. I look at it as a suspension. This is a matter of opinion. It may be merely a matter of definition, but we consider as homogeneous solutions of salt, sugar and that sort of thing, where osmetic phenomena are measurable, but conceive of a state of heterogeneity where the particles of suspended matter are almost infinitely small or ultra-microscopic in the case of colloids. That, I think, applies to most, if not all, colloidal solutions.

Dr. E. W. Smith: I would like to ask a question as to the precipitation of mud in the practical application of this process to the purifying of boiler feed water. Is mud a positive or a negative colloid?

Dr. Whitney: "Mud" is rather indefinite. Mud may be a positive or negative colloid. But that is an interesting question you raise. Prof. Carl Barnes has shown that mud precipitated in the mouth of rivers—the deltas—is precipitated not because the water slows up in its motion, but because salt water comes in and coagulates it.

Dr. A. W. Smith: An aluminum salt would be more efficient as a coagulant than lime or salt water?

Dr. Whitney: Yes, but in the case of this experiment the fact must be taken into consideration that with the lime water a precipitate will form, due to carbonic acid on the water, and this, unless guarded against, will disturb the quantitative results to be expected. When this disturbing effect is removed, it has been shown that the trivalent ions, such as aluminum, are far better coagulants than the divalent ones like calcium.

Dr. J. W. Richards: I would ask Dr. Whitney whether he would regard the solutions of the metals in liquid ammonia, such as were produced by Cady and reported by Brown, as colloidal solutions of the metals?

Dr. Whitney: I do not like to express an opinion there, because I really have none. There will be some papers read at the next meeting of the American Chemical Society on that general subject, and I do not know enough about it to have an opinion.

Dr. Richards: I asked because it is a question whether those solutions are colloids or not, and they conduct current very well, and in every respect like metallic conductors, with a negative temperature coefficient and without any of the usual phenomena of electrolysis.

Mr. Chas. A. Kraus: Since the question has been raised, I may state that there is little probability that the solutions of the metal-ammoniums are colloidal, for the reason that they exert osmotic pressure. In fact they exhibit all the normal solution effects of a solution of sugar in water.

Mr. S. S. Sadtler: Has heat much of an influence in coagulation in precipitating hydrogen sulphide? On boiling the solution, material held in colloidal suspension frequently comes down.

Dr. Whitney: If you can surely eliminate the electrodes it does not cause coagulation. The temperature has an enormous effect, apparently, on the action of the electrolytes.

President Carhart: I am sorry to leave so interesting a subject; but I think we shall have to pass on to some of the other papers.

A paper read at the Seventh General Meeting of the American Electrochemical Society, held at Boston, Mass., April 27, 1905. President Carhart in the chair.

AN ELECTROLYTIC SWITCH.

By William Smith Horry.

The various properties of the aluminum cell are, besides its assymetric peculiarity, that it presents a high resistance to the passage of an electric current, it possesses capacity and it leaks. These qualities may be turned to account for the purpose of preventing those arcs that occur when a circuit, possessing inductance, is interrupted.

As all continuous current circuits possess inductance more or less, the voltage rises across the break when a switch on such a circuit is opened. This not only causes an inconvenient flash at the switch, but endangers the insulation. Field coils of electric motors are sometimes destroyed from this cause. It can be shown that in the small magnet exhibited here, which takes 3½ amperes at 110 volts, the rise of potention is over 400 volts when its current is suddenly interrupted.

But if a suitable electrolytic cell be inserted across the break and the circuit then broken, there is no flash at the switch, and the increased voltage will force a current through the cell instead. The insulation of the cell then breaks down but quickly re-establishes itself. After that the mains may be entirely disconnected without any spark.

To obtain the best results in this way an electrolyte for the cell should be chosen that substantially shuts off all current at the working voltage but that allows considerable leakage to occur with any increased pressure, a cell that has a critical voltage a little above the line voltage. Other matters have to be considered, the conditions being different from those ruling when the cell is to be used for other purposes. For small cells intended for use on circuits of one horse-power or less at 110 volts the matter is not of much importance, but for larger ones it becomes so, as

the electrolyte largely determines the size of the cell required for any given circuit.

The most simple diagram of the circuits is that shown in Fig. 1. The circuit is represented as a line containing an electro magnet, there is a double pole switch for the line, a rheostat contact and an aluminum cell. If the switch is closed no current will flow except that which leaks through the cell, but if the rheostat arm is moved to the left, then the full current will pass. To shut off the current the rheostat is returned to the position shown, then the switch is opened.

But the cell possesses capacity, and, if it be a large one intended to suppress a powerful arc, there will be a spark at the arm con-

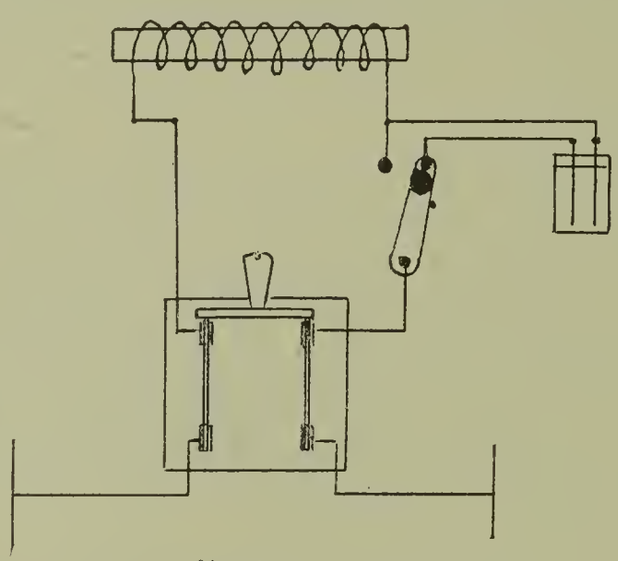


Fig 1.

tacts when the terminals of the cell are connected. To make the circuit sparklessly the rheostat must be moved before the switch is closed. If the arm be moved first, both in opening and closing the circuit, there will be no spark at make, due to capacity, and no arcing at break, due to self-induction.

The switch exhibited operates in this way with one movement of the switch handle. There are three knives to it, the middle one having a more extended movement than the other two, so that it operates always in advance of the outer blades.

Figure 2 is a diagram of the circuits.

The switch is now shown in operation both with and without the aluminum cell, and it will be seen that there is quite a flash unless the cell is used. If the room were dark we could see small

arcs between the plates when the break occurs, and the whole surface of the anode would glow with phosphorescent light. The circuit, instead of discharging at the switch, discharges through the cell, dissociates some of the electrolyte, and generates a little heat.

A small cell of aluminum is sufficient to suppress a considerable flash when employed in this manner, and on the circuit exhibited, and under certain conditions, a cell containing but 9 square inches will do the work. If this suppression of the arc is the only object sought, as at low voltage it would be, a small cell would be employed. But for the purpose of protecting the circuit against high voltages, something larger than the smallest spark stopping cell is necessary.

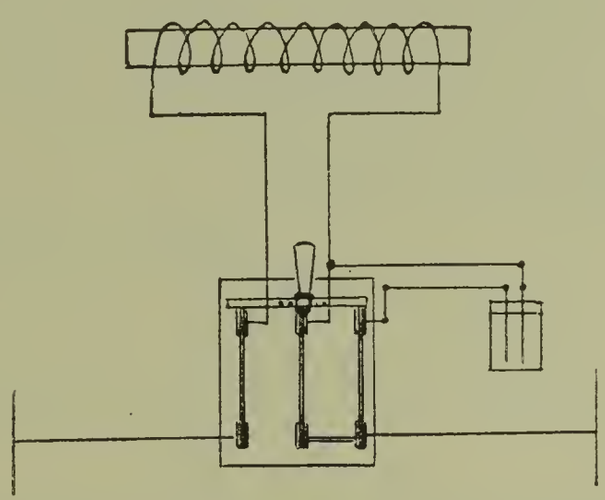


Fig 2

Two cells were made, containing 12 and 24 square inches of aluminum, respectively. The smaller one leaked .01 and the larger .02 amperes at 100 volts D. C. With a certain circuit of 3 amperes broken in the ordinary way there was, of course, an arc, and the voltage ran up to 350 +. When the smaller cell was used with this switch in the same circuit, there was no arc at the break, and the maximum volts were only 250 +. With the larger cell, tried in the same way, the volts were but 149 +. These readings were obtained by setting the voltmeter needle in certain positions, free to move upwards, then breaking the circuit. With the voltmeter disconnected the maximum voltage would be higher than here given, but for all that, the protective property of the cell on the circuit is clearly shown.

By using a much larger cell the voltmeter showed a rise of potential of only 10 volts above the line.

If it is desired that the maximum voltage on a certain circuit, the field of an alternator for instance, shall not rise above 1½ times the applied voltage, then the proper size of the cell can be easily found.

A cell containing 184 square inches of plates was found to break sparklessly such a circuit taking one E. H. P. at 110 volts with a rise of potential to 175 + at the break. Smaller currents seem to require proportionately less plate surface, probably because the resistance of an arc is greater when the amperes are low. In the apparatus shown the cell contains 52 square inches of plates, the electrolyte is sodium phosphate, the leakage about .1 ampere. The magnet takes 3.5 amperes at this voltage, and the maximum volts at the break are 175. From this it would appear that the size of a cell to protect both the switch and the circuit is of reasonable dimensions.

Slow operation of the switch is desirable. A magnet becomes an electric generator while it is losing its magnetism, and a sparkless break is not possible while this induced current is flowing through the cell, which also requires time to reinsulate itself. There is no spark from this cause unless the switch is pulled out quite rapidly.

If the cell be left unused its insulation slowly diminishes, but if used once a day that tendency can hardly be noticed. It was found that both the little cells above alluded to regained their insulation after 17 days' rest in about four seconds, so that after this long rest a sparkless break can be made if the final break be made four seconds after the middle break. On the other hand, the cell insulation increases with frequent use up to the critical point. These properties hardly detract from the value of the device for protecting the circuit. The first break after a protracted rest is always unattended with a high maximum voltage if a second or so elapses before the final break is made, while for continued use necessitating many breaks a minute, the cell heats so that it automatically keeps its resistance from becoming too high. For long continued and rapid use a larger cell is necessary than for infrequent use, so that the heat generated by the continued arcing through the cell shall be radiated more rapidly.

The connections between the switch and the cell should be of low resistance and non-inductive. If an ampere meter be inserted between them, the discharge current may select the path by way of the air gap at the switch rather than by the cell with its added impedance.

It is not essential, of course, that both anode and cathode should be of aluminum; indeed, for large cells it is better theoretically to have the cathode of some other material to reduce the resistance. But it is generally convenient to have both plates the same to simplify the chemistry of the cell, and both plates formed to obviate the trouble of testing for polarity.

This subject has been approached with some hesitation because of its timeworn nature. It was thoroughly investigated by Faraday over 70 years ago, and much has been written on the matter of spark prevention since, so that it would seem that every experimenter in this line has considered it at one time or another. Yet the writer knows of no other device that acts in quite the same way or that is so generally applicable for the purpose of circuit protection as the aluminum cell.

DISCUSSION.

President Carhart: Mr. Horry's paper is open for discussion.

Dr. J. W. Richards: The suggestion comes to me that in using instruments in circuit for measuring the current, the use of the cell simply for the protection of the instruments, where the instrument is to be used near its upper range, would be a useful protection to prevent them from being overloaded when contact is made.

Mr. Horry: It might be if you had a very small cell. A large cell would leak so that it would hardly protect the voltmeter.

A paper read at the Seventh General Meeting of the American Electrochemical Society, held at Boston, Mass., April 27, 1905. President Carhart in the chair.

PRODUCTION OF SILICON IN THE ELECTRIC FURNACE.

By F. J. Tone.

The reaction between silica and carbon when heated in the electric furnace is most interesting, because of the variety of products that may be formed by varying the conditions of the reaction. Starting with the same mixture of these two materials, it is possible to obtain siloxicon, amorphous carborundum, metallic silicon, amorphous silicon, crystalline carborundum and graphite, the formation of each of these respective products being dependent on the temperature of the reaction, the distribution of heat, and, to a certain degree, on the proportions of the constituents of the charge and the intimacy of the mixture.

In any mixture of carbon and silica, the first products to be formed when the charge is heated to the temperature at which silica begins to reduce are silicon-oxygen-carbon compounds in which these elements may be combined in various and most complex proportions, the compounds being at the same time intimately associated with free carbon and free silica. Typical of these silico-carbides are siloxicon and amorphous carborundum. When the mixture consists of one molecular equivalent of silica to two of carbon, and the temperature is reached at which silica is completely reduced, the product, under proper conditions of heating, is silicon. When the mixture consists of one molecular equivalent of silica to three of carbon, and the temperature reaches a still higher point, the product is crystalline carbide of silicon or carborundum. If the temperature be still further increased a point is reached at which carborundum dissociates, the silicon being vaporized and the carbon remaining as graphite of an especially pure and soft variety. When volatilized silicon, formed either from elemental silicon or dissociated carborundum, is expelled from the furnace, it is generally oxidized upon coming in contact with the air, forming silica. In cases, however, it is condensed in the form of a brown vitrious product containing a considerable

proportion of amorphous silicon. All of these products require for their formation close control of temperature and careful distribution of heat; and especially is this true in the production of silicon, the commercial manufacture of which has offered great difficulties. It is my purpose to describe a process for the manufacture of silicon in which these obstacles have been successfully overcome.

Silicon belongs to a class of elements whose temperatures of reduction and volatilization are comparatively close, and since, unlike iron and other baser metals for instance, its reduction is accomplished in a furnace capable of generating much higher temperatures than that required for the simple reduction of the ore, the control of temperature and the distribution of heat become paramount considerations. To meet these conditions the resistance type of furnace is employed, in which the resistor is an independent carbon conductor of comparatively large radiating surface, placed vertically through the charge. If an arc furnace were used, the heat would be localized in a small area and large amounts of the metal would be vaporized as soon as formed, resulting in a considerable loss of product. The arc type of furnace, therefore, is not adapted for carrying out the reaction in an efficient manner. It is necessary for the economical reduction of silica to silicon that the proper temperature shall at no point be greatly exceeded, and that the product shall be removed as soon as possible from the reduction zone. These conditions are very satisfactorily met by a resistance furnace of the type referred to.

The furnace structure consists of a vertical cylindrical chamber open at the top, the containing walls being built of fire brick. The charge consists of silica in the form of silica sand, analyzing about 99.5 per cent. silica, and carbon in the form of finely pulverized foundry coke. These are mixed in the proportion of 60 parts silica to 24 parts carbon, as determined by the equation

$$SIO_2 + 2C = Si + 2CO$$

It has been found of great importance to have this mixture made in the most thorough manner possible, in order that when the temperature of reduction of silica is reached there may be in proximity to every grain of silica the exact amount of carbon

necessary to accomplish reduction. Either an excess or a deficiency of carbon will tend to form other products and lower the efficiency of the process. Through the center of the chamber, and surrounded by the charge, is placed the vertical carbon resistor, joined at the base and at the top of the furnace to carbon terminals, which are connected to the source of electrical energy. In order that there may be no localization of heat, but the best possible distribution of the same, the core is made with a large radiating surface; and, in order that the silicon may be removed from the reaction zone as soon as it is formed, the resistor and likewise the reaction zone are disposed in a substantially vertical direction. Thus the charge, in its progress through the reaction zone, takes a downwardly vertical path and the removal of the product is readily accomplished by gravity. The features of this furnace construction, therefore, are the large area of the reduction zone and the vertical disposition of the resistor. By means of the first, the delicate temperature regulation is easily accomplished, and by means of the second there is afforded a method by which the particles of silicon may, as soon as they are formed, fall by gravity out of the zone of reduction and thus escape volatilization.

When current is passed through the resistor and the temperature is reached at which silica begins to reduce, the charge in proximity to the core is converted into the various silico-carbides which are characteristic of the initial heating. As heating progresses there are found in this product numerous molten particles of silicon held in suspension by the unfused partially reduced charge. As these particles coalesce and form larger globules, they are enabled to flow through the charge and fall to the lower part of the chamber. When a sufficient amount has collected, the fused product passes out into the receiving space below and may be tapped and cast into pigs and other forms. The process may thus be conducted in a continuous manner.

Silicon produced in the electric furnace is a crystalline body, generally quite dense and of dark silver luster. Compared with the metals, it is quite brittle and stands between six and seven in the scale of hardness. The specific gravity of the commercial product is 2.34, and its melting point 1,430° C. At white heat and even at a temperature as high as 1,300° C. it is not oxidized

in the air. At temperatures somewhat below its melting point it is readily oxidized. The specific resistance of silicon is very high and it also has a high temperature coefficient.

A typical analysis of the commercial product is as follows:

Si	95.30
Fe	1.06
Al	1.61
C	2.10
CaO	.33
	100.40

The principal impurities are iron and aluminum, and these can be mostly eliminated, if desired, by the use of charge composed of pure crude materials.

If extended use is to be made of silicon in the arts, its most important application will no doubt be in the metallurgy of steel and copper. Silicon, as is well known, is a reducing agent of great power. The use of high silicon alloys in the manufacture of steel castings has now become very general, and it has been found that as the content of silicon in the ferro alloy has been successively increased from 25 to 50 per cent., and finally to 75 per cent., the steel has likewise improved in quality and uniformity. When the pure metal is used, it is in the form to exert its greatest possible reducing action per unit of silicon, for the reason that, being initially uncombined with iron, it is free to at once react on the oxides in the bath. In the manufacture of copper and brass castings, pure silicon is used in the same manner and for the same purpose as silicon copper.

An interesting application of pure silicon is that analogous to the use of aluminum in Goldschmidt's alumino-thermic process. The heat of formation of SiO_2, representing the oxidation of 28 grammes of silicon, is 219,000 calories. The heat of formation of Al_2O_3, representing the oxidation of 54 grammes of aluminum, is 389,000 calories. It will be seen, therefore, that, gramme for gramme, silicon generates slightly more heat than aluminum. Silicon, however, requires about one-third more oxygen for its combustion than aluminum; and in a mixture of silicon and ferric oxide in proper proportion to duplicate the alumino-thermic

reaction, although this reaction is initiated without difficulty, the heat generated per unit of mass of mixture (or, as it has been expressed, the energy density) is somewhat less with silicon than with aluminum. Silicon, however, has certain advantages in that, unlike aluminum, it is brittle and can therefore be easily pulverized. At reduced prices it may find an application in this unique field.

Silicon as anode has been tried in chloride solutions, but without successful results. It is rapidly oxidized to the gelatinous H_2SiO_3.

The high electrical resistance of silicon, and also its resistance to oxidation even at white heat, readily suggest uses for it as an electrical resistance material.

The reaction of mixtures, powdered silicon and oxygen compounds which freely give up a portion of their oxygen, is very violent. It has been proposed that, mixed with potassium chlorate, ammonium nitrate or similar compounds, it will form a powerful and valuable explosive.

It may be interesting in this connection to further mention the product which is formed under certain conditions of operation and which contains a considerable proportion of amorphous silicon. When portions of the furnace charge are too highly heated, volatilized silicon is expelled from the furnace. If this vapor comes freely into contact with the air it oxidizes to SiO_2 in dense white fumes. In cases, however, probably due to deficiency of oxygen, there is found on exposed portions of the charge a brown vitreous substance consisting principally of a homogeneous mixture of silica and amorphous silicon.

Considerable analytical work has been done on this product by Mr. E. D. Thebaud, and it was first assumed, on account of the homogeneous character of the substance and the relative proportions of silicon and oxygen, that it was monoxide of silicon. This view has since been found to be erroneous, and the fact is mentioned here simply as being further ground for the belief that the compound silicon monoxide does not exist. Certain experimenters have described the occurrence of this suboxide, but it may be noted that, in the operation of the silicon furnace, neither the incomplete reduction of silicon dioxide nor the partial oxidation of silicon give a product which can be identified as silicon monoxide.

This product containing amorphous silicon analyzes as follows:

Si (amorphous)	27.05
SiO_2	65.97
C	4.90
Fe_2O_3	.42
Al_2O_3	1.26
CaO	.40
	100.00

It is very brittle, is apparently without crystalline structure, and has a specific gravity of 2.22 at 24° C. It is a non-conductor of electricity. Treated with cold hydrofluoric acid, the silica is readily dissolved, leaving amorphous silicon in a finely divided state. The inference might be drawn that under proper conditions the condensation of the vapor of silicon results in the production of the amorphous form.

DISCUSSION.

President Carhart: The paper is open for remarks or inquiry.

Mr. H. N. Potter: I might say that silicon seems to be superficially oxidized by carbon dioxide at temperatures attainable in a muffle furnace heated by gas, so that after so heating, the surface shows a play of colors like tempered steel.

Dr. Elihu Thomson: I have been very much interested in the development of silicon manufacture. A number of years ago we obtained about two ounces of crystallized silicon by the ordinary chemical methods, and the possibility of getting this element on a large scale is to my mind a very important development. Silicon will melt in high furnace temperatures so that it can be cast to form. One can get any shape one wishes of silicon. As a resistance rod standing high temperatures, it seems that there is a possibility of great usefulness.

It also makes an excellent resistance column when granulated or powdered and put into an insulating tube under variable pressure. We actually find that the resistance can be made to range

down from about 500 to 1, by mere increase of pressure, and the original resistance is restored by releasing the pressure and slightly tapping the tube which contains the silicon. If the current, however, is continued at too high a value, the fall of resistance is very rapid. A critical point is reached, and on examining the granules after the experiment, they are found to be partly fused together in the interior of the mass. In other words, it is necessary to run such a resistance with sufficient cooling to prevent the interior temperature rising too greatly. The investigation of the variations of resistance at increased temperatures of silicon seems to show that the resistance rises up to a certain point —about the melting point of silver—and then drops rather rapidly up to its own fusing point.

As an interesting matter in this connection it may be mentioned that a few days ago we took out a sample of silicon from a crucible, which sample had attached to it crystalline masses which, under the glass, apparently resembled carborundum. When I add that the silicon was melted in a graphite crucible you can easily see where the carbon came from. A combination seemed to take place at ordinary heats, and the crystals were in every way, so far as we can determine, identical with those of carborundum.

Prof. Franklin: I would like to know what the specific resistance of silicon is, as compared with carbon.

Dr. Thomson: I think, if I remember rightly, it is about three times that of carbon.

Mr. Potter: I wish to claim for Mr. Albro the discovery of certain heat liberating, self-propagating reactions between silicon and oxides, denied, I believe, by Dr. Goldschmidt. In view of the patent situation I cannot say more at this time, except to state that the name *"Calorite"* has been given to a reactive mixture of silicon and an oxygen supplying compound.

President Carhart: There appears to be in the silicon granules a sort of coherer action.

A paper read at the Seventh General Meeting of the American Electrochemical Society, held at Boston, Mass., April 27, 1905. President Carhart in the chair.

THE MICROSTRUCTURE OF SILICON AND ALLOYS CONTAINING SILICON.

By A. B. Albro.

INTRODUCTION.

This paper is written, not to propose or to defend any theories, but to show photographically recorded facts.

Enough discordant theories regarding the effects of silicon upon metals have already been advanced. For example:

(a) Von Jonstorff[1] claims that increasing the silicon in steel increases its brittleness, while Hadfield[2] states that 2 per cent. of silicon with about 1 per cent. of carbon increases the toughness of the steel considerably.

(b) Carnot and Goutal[3] state that silicon usually exists free in cast iron, and that any silicide formed in the furnace disappears on cooling the iron, and in proof of their claims quote the results of Le Chatelier's[4] experiments on the electrical resistance of steel and iron containing silicon, while Stead[5] states that silicide of iron dissolved in iron is one of the constituents of the phosphoric eutectic in gray silicious pig-irons.

Others might be quoted regarding the effect of silicon on the properties of the phosphoric eutectic, the melting point and fluidity of cast iron and steel, and various other properties of iron and its alloys, but the above serve to show the considerable disagreement among authorities.

In contrast with this, the belief that silicon reduces the percentage of iron carbide in pig-iron is universally held. Moissan's[6] concise statement of this phenomenon is as follows:

[1] Report presented at Third International Congress of Chemists at Vienna. Stahl und Eisen, March 1 and 15, 1899.

[2] Reprint of paper read at Institute of Civil Engineers. "The Metallographist," Vol. I, pp. 135, 136.

[3] "Annales des Mines," October, 1900.

[4] Translation in "American Manufactures," Feb. 12, 1903, from Comptes Rendus.

[5] "Journal Iron and Steel Institute," 1900, No. II.

[6] Moissan, "Electric Furnace," Eng. edition, p. 69.

" . . . silicon displaces carbon in iron and iron carbide. These bodies when maintained at sufficient temperature behave exactly as the aqueous solution of certain compounds in which we precipitate or displace substances in solution or combination. If the displacement of the carbon is not entirely complete a state of equilibrium is established between the silicide and carbide of iron, an equilibrium in which the conditions vary with the temperature and with the impurities which are contained in the bath. This is generally the case with white or gray cast-iron."

Most investigators agree that the presence of silicon lessens the liability of blow-holes, and thus promotes soundness in cast-iron and steel, but they differ greatly as to how this result is attained.

Undoubtedly some of the diversity of opinion concerning the effects of silicon is due to certain observers attributing to it the bad qualities of its oxy-compounds.

Iron containing up to about 14 per cent. silicon can be produced in blast furnaces.

The electric furnace is capable, under proper conditions and expert manipulation, of producing ferro-silicon of any percentage composition, and recently silicon practically free from iron has been produced in commercial quantities by the reduction of silica by calcium carbide or by carbon.

In Europe the process of Scheid is in operation, while in this country the work of Mr. Tone has recently attracted considerable attention.

A novel silicon process has been devised for Mr. George Westinghouse by Mr. Henry Noel Porter, under whose direction these investigations were made.

SILICON.

The first slide shows graphitoidal silicon magnified 23 diameters. This sample was furnished by Mr. Frederic S. Hyde, and was from the original material made by him and described in his article on graphitoidal silicon.[7] To the unaided eye it has the appearance of coarse graphite flakes, and in this slide is seen to consist of irregular shaped masses, some of which have plane surfaces.

[7] Journal Am. Chem. Soc., Vol. XXI, No. 8, August, 1899.

The silicon needle-like crystals next shown (Fig. 2) were also furnished by Mr. Hyde, and are here magnified 34 diameters. These needles were made by solution and crystallization in molten zinc. The actual length of these crystals is about one millimeter.

Fig. 3 shows three complex crystals of pure silicon, magnification, 23 diameters, made by dissolving pure silicon in molten zinc. The pure silicon was obtained from crystalline silicon which had been very finely powdered and then purified and washed. Only the particles which remained in suspension for forty-eight hours were used. The resulting powder analyzed 99.8 per cent. silicon, gave absolutely no gritty sensation when placed between the teeth, and showed very few crystals under a magnification of 205 diameters.

These complex crystals resemble very much the dendrites of alpha iron shown and described by Osmond and Cartaud.[8] Their actual length was from 1.5 to 2.5 millimeters. The same zinc solution also contained single octahedra of silicon.

When fused in the electric arc furnace, silicon collects in the fluid phase and in its subsequent solidification extrudes some silicon in the form of worm-like nodules. The surface of these nodules exhibits fern-like crystals, and Fig. 4 shows them magnified 8 diameters. Single crystals have been observed which measured 15 by 50 millimeters.

Before passing to the internal structure of silicon, a word regarding the method of preparing sections for examination is in order. Samples are ground on a carborundum wheel until the desired section is reached, and then ground to a plane surface on a glass plate with "'FFF'" carborundum powder and water. The last stages of preparation are like those of ordinary steel sections. Etching is done with dilute mixed hydrofluoric and nitric acids in the case of all silicon sections, but the etching acid differs with alloy sections, and will be stated for each one.

In the case of silicon there is a difference between the appearance of a section cut vertically and one cut horizontally through a mass or nodule, and it is, therefore, necessary to know how the mass lay while cooling and to state which sections are vertical and which horizontal.

All photomicrographs having a magnification less than 167

[8] "Annales des Mines," August, 1900.

diameters were taken with oblique light, the higher enlargements with vertical illumination. The source of light was a single-glower, fifty candle-power Nernst lamp, with globe removed. This gives a very even illumination of such intensity that with a 1-6-inch objective and 2-inch eye-piece, the exposure necessary with Seed "L" orthochromatic plates ranges from 10 to 60 seconds.

Fig. 5 shows a vertical section of a nodule strongly etched and under a magnification of five diameters.

Fig. 6 shows a horizontal section of a nodule strongly etched, and then repolished to bring out only the division lines between individual grains. This shows clearly where impurities at certain places between the grains have been etched away. Magnification, eight diameters.

Fig. 7 shows a slightly etched vertical section of a similar nodule, and Fig. 8 a horizontal section under the same treatment. The dark areas in No. 8 are actual blow-holes, and no nodule was found whose central horizontal plane was free from them. Magnification in both cases, eight diameters.

A peculiar formation noticed in one case under a magnification of 89 diameters is shown in Fig. 9. It is a slightly etched vertical section of a nodule which had been twisted once around its horizontal axis during the formative period.

Owing to the fact that the nodules are under stress during freezing, the crystalline structure is probably distorted, and we should expect to find an undistorted structure only in sections taken from an unstrained mass in the interior of a large block of material.

The next few slides show such interior sections under different magnifications. They are from three samples of silicon called A, B and C.

Sample A was from a 500-pound lot purchased in France in March, 1904, and contains 92.6 per cent. silicon, the balance being mainly calcium, iron and aluminum.

Sample B was very kindly furnished by Mr. Frank J. Tone, of the Carborundum Company, Niagara Falls.

Sample C was made by Mr. Potter, and contains 98.8 per cent. silicon, the balance being iron and aluminum.

The next two photomicrographs show Sample A magnified 8

diameters. No. 10 is a vertical section showing the junction of two masses partially fused together. Long, irregularly overlapping and interlocking grains are seen, many of which seem to have two faces shown in this section.

In No. 11, which is a horizontal section, these apparently two-faced grains are shown more clearly, and several triangles are formed by them. In this appearance the section resembles to a striking degree the fern-leaf surface crystals shown in Fig. 6. In addition to these, several of the interlocking grains can be seen, but very much shorter than in the vertical plane.

This difference in length of grains viewed vertically and horizontally tends to explain why large masses of silicon fracture much more easily in the plane vertical to the surface uppermost during solidification. It is practically impossible to produce two parallel fractures in the horizontal plane, while this can be readily done in the vertical plane.

Fig. 12 shows a horizontal section of Sample B magnified 8 diameters. This is seen to consist of two large, irregular-shaped grains, together with several smaller ones. In the neighborhood of the smaller grains, silicon carbide crystals are seen.

Sample C, next shown (Fig. 13; 8 diameters), is characterized by its large grains, it being impossible to include a complete grain in the field, 7.6 mms. in diameter, covered by this photograph. The interlocking of the grains is very clearly shown, as well as their homogeneity and the absence of any impurities between them.

The next three slides show horizontal sections magnified 34 diameters.

No. 14 is Sample A, and shows the interlocking grains and impurity pits. No. 15 is Sample B, and shows a smooth homogeneous field with the exception of the three areas containing silicon carbide. No area could be found which was free from this compound. In No. 16, which is Sample C, a remarkable interlocking of the two dark grains with the H-shaped light grain is shown. The field shows such great homogeneity that it can safely be called a photomicrograph of absolutely pure silicon.

The ultimate structure is approached in the next three slides, in which the three samples are shown magnified 167 diameters. Fig. 17, Sample A, shows a very close-grained surface with

some octahedra in various portions, but the structure has not the clearness that purer silicon possesses.

In Fig. 18 we have Sample B, and this shows a field of pure silicon, with one area containing silicon carbide. Individual crystals can be distinguished here, together with numerous striated areas.

Sample C, as shown in Fig. 19, shows the structure more clearly than No. 18, and at the same time is free from any impurities. Numerous octahedra and clearly striated areas are visible.

With this latter section under a magnification of 1,025 diameters, as shown in Fig. 20, we have the characteristic silicon crystal. Despite the slight lack of clearness, octahedra are clearly shown which are striated on the surface, the striations overlapping each other like shingles on a house, the same structure as Stead observed in his sample of steel containing 4 per cent. of silicon.[9]

The structure of silicon does not appear to be affected by any temperature below its freezing point, as the grains and crystals have the same appearance when quenched at a bright red heat as when the cooling occupies twenty-four hours.

This may explain why the structure of steels containing 4 per cent. of silicon is unaffected by heating to 1,100° Cent., as stated by Stead[10] and others.

FERRO-SILICON.

In the steel industries silicon is used in the form of an alloy with iron under the name of ferro-silicon.

With the exception of two samples purchased from Messrs. Eimer & Amend, New York, all ferro-silicons used were made especially for this investigation. In these the silicon content ranged from 30 to 88 per cent., but as ferro-silicon is generally sold under three classifications, viz., 25 to 30, 50 to 55, and 70 to 75 per cent. silicon content, only these grades of the alloy are shown and described herein.

The physical structure of these grades of ferro-silicon is very interesting. As the percentage of silicon increases from 30 to 50 the brittleness of the alloy increases rapidly, and the 50 per cent.

[9] Reprint of paper read before Iron and Steel Institute, May, 1898. "The Metallographist," Vol. I, pp. 327, 328.

[10] Iron and Steel Institute, May, 1898.

alloy can be crushed between the fingers to octahedra about one-half a millimeter on an edge. After 50 per cent. is passed the ease of fracture remains practically the same in the vertical plane, but becomes more and more difficult in the horizontal plane. After 75 per cent. is passed the fracture becomes more difficult in both planes until the peculiarities noted with 92 to 98.8 per cent. silicon are attained.

In the fracture of ferro-silicon containing 60 per cent. of silicon, plates were obtained measuring two centimeters along their vertical axis, with a width of one centimeter and a thickness of from one to two millimeters.

The etching of the ferro-silicon sections was done by immersing the sample in dilute mixed hydrofluoric and nitric acids for ten seconds; washing and drying and then immersing in concentrated aqua regia until details were brought out clearly.

As a basis of comparison, Fig. 21 shows a practically carbonless area of Swedish iron magnified 118 diameters, with vertical illumination.

Fig. 22 shows 50 per cent. ferro-silicon magnified 8 diameters, but does not give the detail presented by this section to the unaided eye, as it then showed distinct laminations running at various angles in different grains.

Fig. 23 is 52 per cent. ferro-silicon, 8 diameters, and shows the large grain formation characteristic of silicon. These grains, like those of silicon, are plainly visible to the unaided eye. The incipient fractures can also be seen.

Fig. 24 shows ferro-silicon having 75 per cent. silicon content, 8 diameters, and shows the approach to the structure of pure silicon. The matrix seems to be composed of octahedra, with incipient fractures extending in all directions between them.

No slide is shown of 32 per cent. ferro-silicon at 8 diameters, owing to the lack of detail. With a magnification of 34 diameters the details of its structure begin to appear, as is seen in Fig. 25.

Irregular areas, surrounded by wide channels which have been etched away, are characteristic of alloys of about this percentage. Continued etching brings out this structure more clearly, but at the expense of flatness of field.

Fifty per cent. ferro-silicon, 34 diameters, is shown in No. 26. Owing to its extremely pulverulent nature it was impossible to

obtain a plane surface for examination, but this slide shows its characteristic crystalline structure, and many octahedra can be distinguished despite the unevenness of the surface and consequent lack of sharpness in the photograph.

Fig. 27 shows 52 per cent. ferro-silicon, 34 diameters. It presents a rough-grained matrix, showing some octahedra and laminæ of silicon. These latter show white on the dark background of the matrix.

With the same magnification, 34 diameters, the 75 per cent. alloy possesses a very characteristic structure, as is seen in Fig. 28. Numerous irregular-shaped interlocking grains of silicon are seen, with the octahedra of the alloy between them and sometimes extending in laminæ of considerable length.

With vertical illumination and a magnification of 167 diameters, 32 per cent. ferro-silicon exhibits a very interesting structure, as shown in Fig. 29. The etching was carried far enough to bring out the details of the matrix, and, as a result, the irregular prominent grains cannot be brought into focus at the same time. The matrix shows somewhat the structure of impure iron, and seems to have grains of silicon imbedded in it at irregular intervals. The prominent irregular-shaped areas, when brought into focus, show the same structure as that of 52 per cent. ferro-silicon with the same magnification, 167 diameters, as shown in Fig. 30.

In this we have the surfaces of two grains and the dividing line between them. The section seems to be homogeneous in structure, with the exception of one or two large irregular grains standing in clear relief above the surrounding material. These probably are grains of silicon.

Fig. 31 shows 75 per cent. ferro-silicon, also 167 diameters. Here we have, in the band running through the center of the field, a structure resembling that shown in the 52 per cent. material of the last slide, while the surrounding portions of the field have a structure resembling impure silicon. The fact that the central band is etched slightly deeper than the other portions would tend to prove this.

These slides show that the structure of iron is decidedly different from that of silicon or any silicide of iron which may exist, and that the presence of silicon or a silicide in iron should be

distinguishable in iron as clearly as that of phosphorus or sulphur. Further, the composition of ferro-silicon can be determined, at least roughly, by means of the microscope with very little practice, and especially when one has only to distinguish between two samples whose silicon content differs by from 5 to 10 per cent. The 30 per cent., 50 per cent. and 75 per cent. can readily be distinguished from each other by their fractures.

COPPER-SILICON.

In studying this alloy three grades of material were used, containing respectively 2.3 per cent., 10.12 per cent. and 23.4 per cent. copper. The 10.12 per cent. silicon copper was furnished from stock purchased by the Westinghouse Electric and Manufacturing Company, while the other two were specially made.

In regard to physical properties these samples differed greatly, the low percentage alloy having almost the same appearance and malleability as ordinary ingot copper, while the high percentage alloy was steel-gray in color, hard and very brittle. The 10.12 per cent. alloy possessed properties intermediate between these two, being silver white in color when freshly fractured and turning to a straw yellow on standing twenty-four hours. The fracture was markedly conchoidal, and in some cases in breaking a piece from the mass it would separate with two and sometimes three cleavage surfaces, all of which were conchoidal.

The low percentage alloy was etched with dilute, the other two samples with concentrated, aqua regia.

Fig. 32 shows 2.3 per cent. copper silicon magnified 34 diameters after prolonged etching. In the large grains two sets of laminæ at right angles are noticeable. In the smaller and darker grain the laminæ are at a different angle and somewhat indistinct. The surface appearance of this alloy to the unaided eye was very striking, presenting irregular polyhedral grains sometimes two or three millimeters across.

Fig. 33 shows the 10.12 per cent. alloy, also 34 diameters. The white areas show the presence of silicon, as they are composed of silica which results from the action of aqua regia on copper silicide, Cu_2Si.

Figs. 34 and 35 show the same sample with vertical illumina-

tion and a magnification of 167 diameters. The dark areas are pits caused by the action of the etching fluid, and are, I believe, copper areas. The main body of the section is made up of minute irregular grains overlapping each other to some extent. Some of these are eaten away more rapidly than others, and are a straw yellow color, while the latter appear white.

The 2.3 per cent. alloys, after being repolished and very slightly etched with dilute aqua regia, had, when magnified 8 diameters, the appearance shown in Fig. 36. This sample shows some scratches on its surface, but has, nevertheless, the same laminated appearance shown with higher magnification in Fig. 32.

As the high percentage alloy showed nothing in addition to that already shown by the 10.12 per cent. copper-silicon, no figures are presented.

THE ACTION OF SILICON TOWARDS CARBON AND SILICON CARBIDE.

The facts recorded in this division of the subject are presented because of the peculiar microstructures and physical properties observed.

Silicon may be melted in a carbon container without introducing carbon or silicon carbide. The next slide (Fig. 37) shows the junction formed between silicon and Acheson graphite under a magnification of 34 diameters. The dividing line is sharply defined, and the silicon is homogeneous in structure, showing no areas in relief, which are always seen when silicon carbide is present.

Fig. 38 shows a cross section of the tip of an arc electrode used in fusing silicon. In this case the silicon was subjected to a very high temperature, and the carbon to the action of silicon vapor. The silicon here, in distinction from the former sample, shows the presence of its carbide, as indicated by the long, narrow, raised portions. However, it will be noticed that the dividing line between the graphite and silicon is still sharply defined, but analysis of the silicon shows no free carbon content, and the graphite can be cleanly cut away from the silicon surface. Magnification, 34 diameters.

Solid carbon and molten silicon do not necessarily react. In the large number of samples examined, made under the greatest range of temperatures, the silicon has never contained any free carbon.

The characteristic silicon carbide crystal is described as a hexagonal plate; in other words, a hexagonal prism in which the shortest axis is the distance between the two hexagonal surfaces. With silicon crystals this axis is generally the longest one, and, when crystals of silicon have been found whose form was that of the accepted silicon carbide crystal, they have been called silicon pseudomorphs of silicon carbide, despite the fact that in the dissociation of the carbide at high temperatures the carbon, not the silicon, remains.

The author has examined many grottoes in silicon in which hexagonal plates have been found measuring from two to twenty millimeters on the longest diagonal. These on analysis were found to be pure silicon, containing no trace of carbon or silicon carbide.

From the powerful influence of silicon on the structure of metals in general, it is probable that it profoundly influences the crystal type of its carbide SiC, about 70 per cent. of which is silicon, and that hexagonal plates of silicon, instead of being silicon carbide pseudomorphs, are merely another form for the hexagonal prisms or octahedra observed as characteristic of silicon.

Fig. 39 shows crystalline silicon carbide magnified 8 diameters. The laminated structure is very clearly seen together with several hexagonal plates. This sample consisted of one large crystal, to which several smaller ones were attached.

Silicon containing about 20 per cent. of silicon carbide presents the peculiar structure seen in Fig. 40. The white portions contain amorphous silicon carbide, while the dark areas are silicon. Magnification, 8 diameters.

Fig. 41 shows this same section magnified 34 diameters, and reveals a softer matrix from which irregular grains stand out in relief. This structure is shown equally well by polishing in bas-relief on cloth or by etching with mixed nitric and hydrofluoric acids.

The next two slides (Figs. 42 and 43) show different sections of the same sample magnified 167 diameters. The large, prominent grains are a silicon-silicon carbide material; while the hexagonal plates are crystals of carbide which have crystalized from solution of the amorphous material in molten silicon. It will also be noticed that the matrix has the characteristic silicon structure.

In addition to the above reaction, Mr. Potter discovered that when silicon and silicon carbide are saturated with each other the resulting material exhibits remarkable properties. Analysis proves this to contain the element and its carbide in proportions approximating very closely the formula

$$SiC + Si = \text{(perhaps) } Si_2C.$$

The material is non-porous, harder than corundum, and so tough that a three-inch cube withstood heavy blows from a sledge on all its faces without fracture. It is evident that this substance, termed by its discoverer "carbosilicon," is very different from either of its components in regard to toughness, and that the method of combining the element and its carbide has much to do with the properties of the resultant substance.

In comparison with the previous slides which showed a solution of amorphous silicon carbide in silicon, Fig. 44 shows the structure of "carbosilicon" under a magnification of 34 diameters. It will be seen to be much more homogeneous than the ordinary solution.

The next two slides (Figs. 45 and 46) show this material magnified 167 diameters. All portions of the mass have the same structure as the parts shown in sharp focus in these photographs. No characteristic silicon structure is visible, only that characteristic of silicon saturated with its carbide or vice versa. Its complete freedom from large grains and the absence of any symmetrical arrangement of the grains obviously accounts for its toughness.

It thus appears that silicon has a remarkable influence upon the structure of anything with which it enters into solution or combination, and further investigation would seem almost certain to be rewarded by the discovery of novel and valuable properties which are particularly alluring in view of the certain cheapness of silicon as soon as a demand develops.

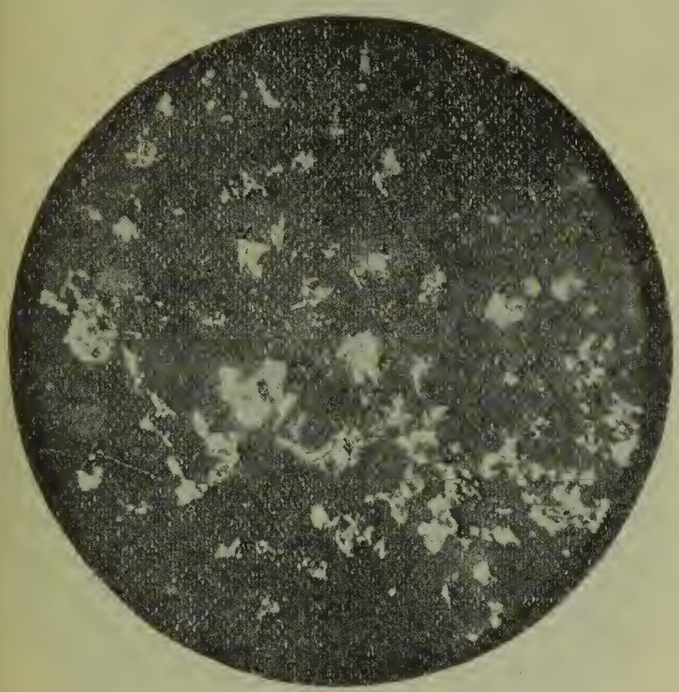
These studies were made at the suggestion of Mr. Potter, and I wish in conclusion to express my great indebtedness to him for his direction and counsel throughout.

NOTE.—After the completion of the photomicrographs for this paper, two samples of ferro-silicon were received from the Roessler & Hasslacher Chemical Company, New York, according

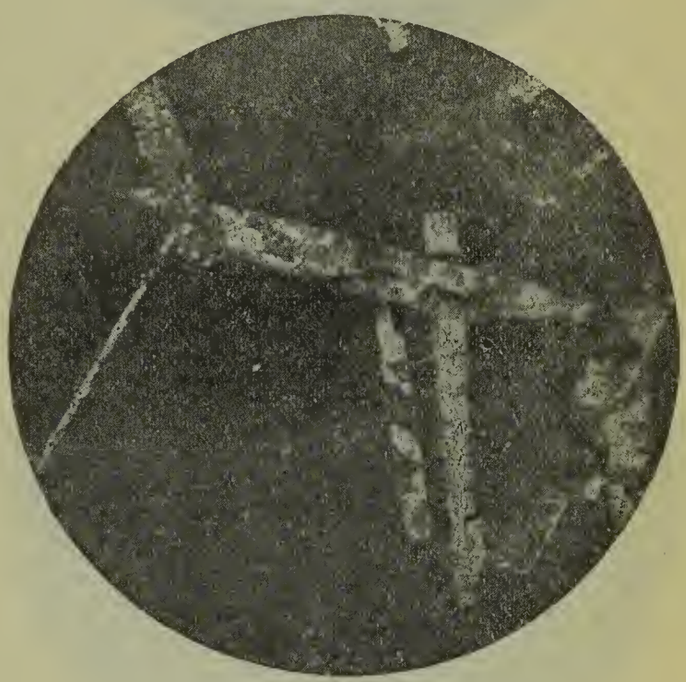
to their analysis containing 57.78 and 75.60 per cent. of silicon, respectively.

Their appearance, fracture and microstructure are the same as samples of like composition made especially for this paper.

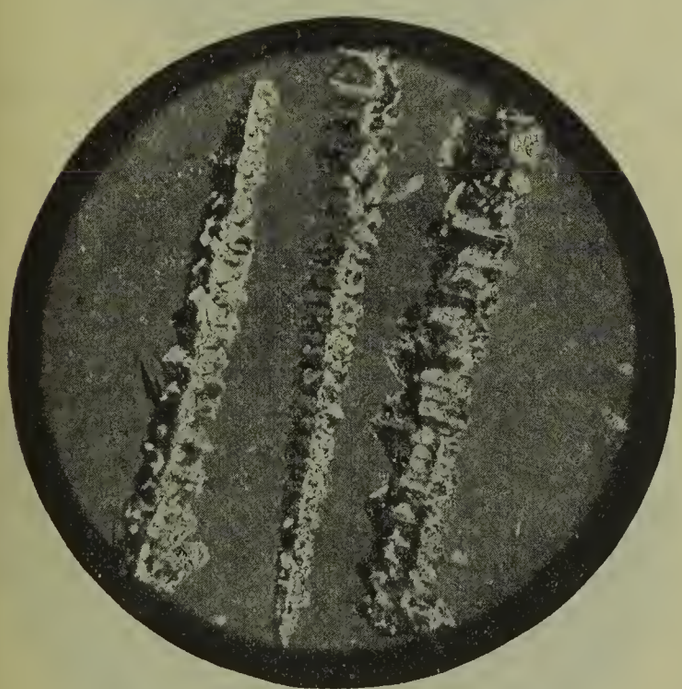
The microstructure of the 75.60 per cent. material is characteristic, while that of the 57.78 material shows the distinguishing octahedra of 50 per cent. ferro-silicon, with intergranular areas of silicon.



No. 1. Graphitoidal Silicon x 23.



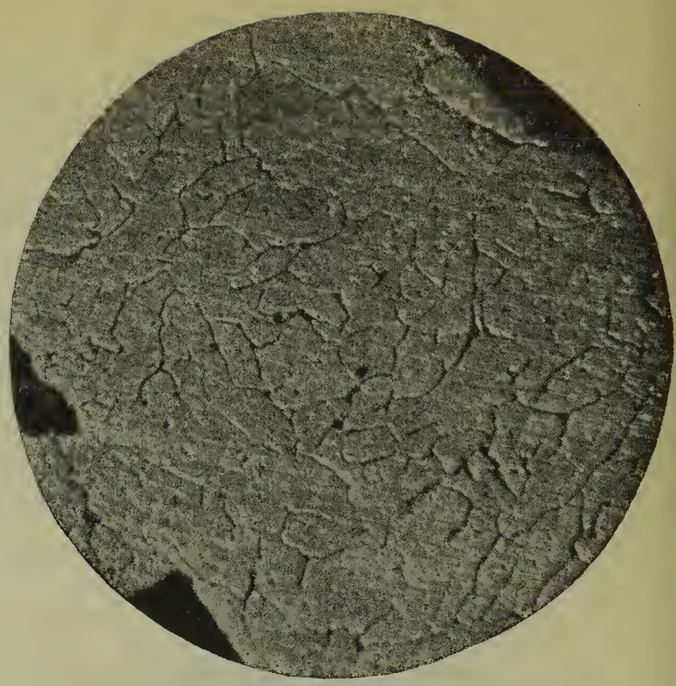
No. 2. Silicon Crystals, x 34.



No. 3. Silicon Crystals, x 23.

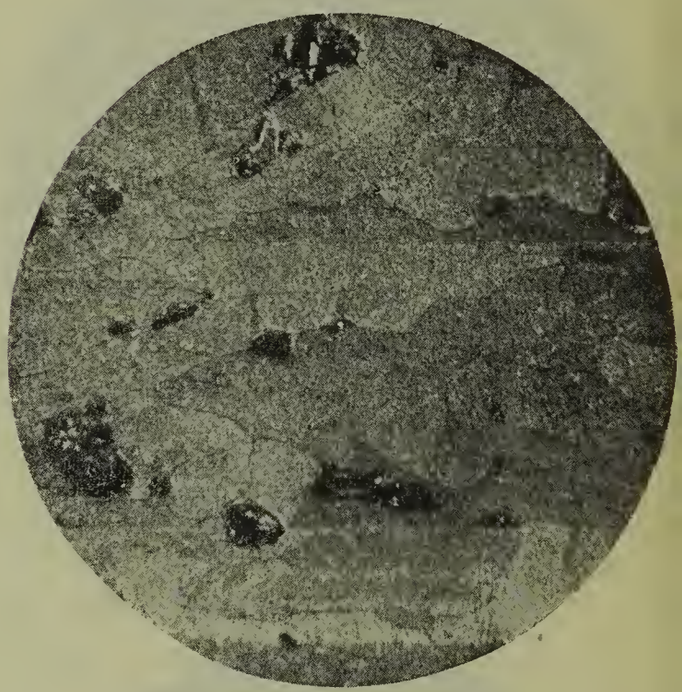
No. 4. Silicon Surface Crystals, x 8.

No. 5. Silicon Nodule, x 5.



No. 6. Silicon Nodule x 8.

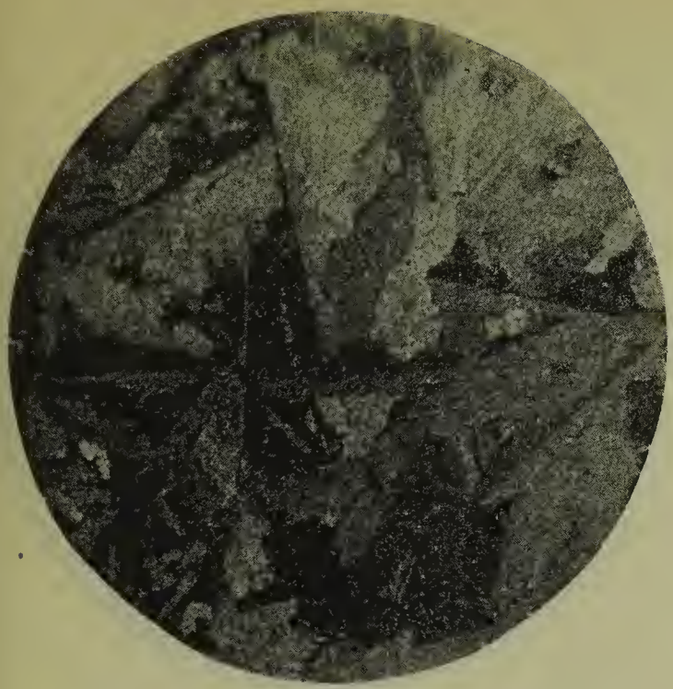
No. 7. Silicon Nodule, Vertical Section x 8.



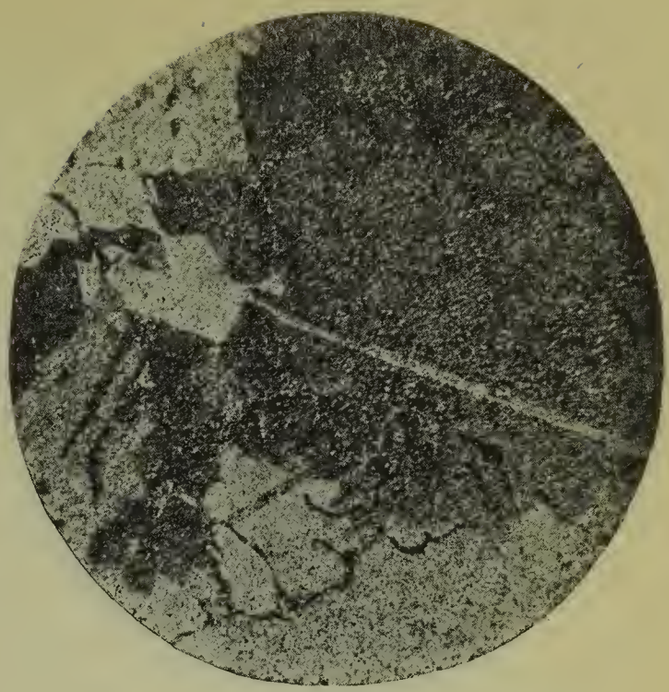
No. 8. Silicon Nodule, Horizontal Section x 8.

No. 9. Distorted Nodule v x 89.

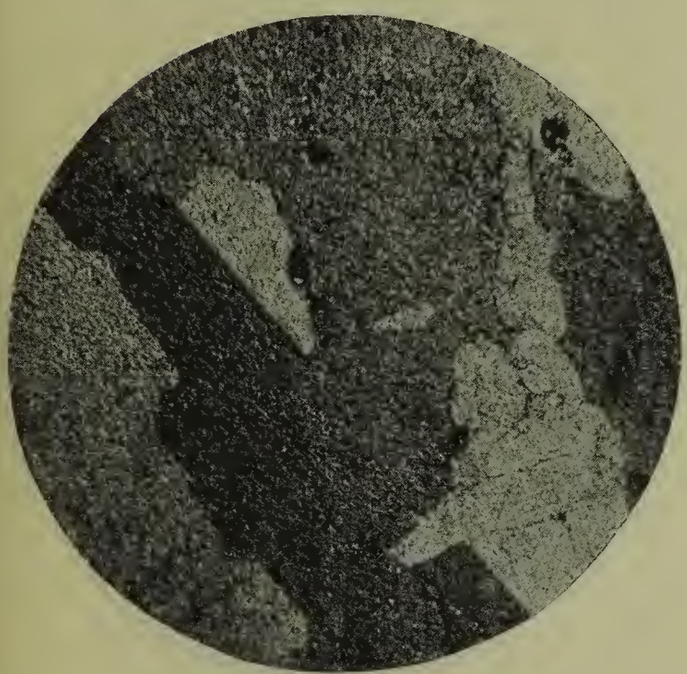
No. 10. "A" Silicon-vertical section, x 8.



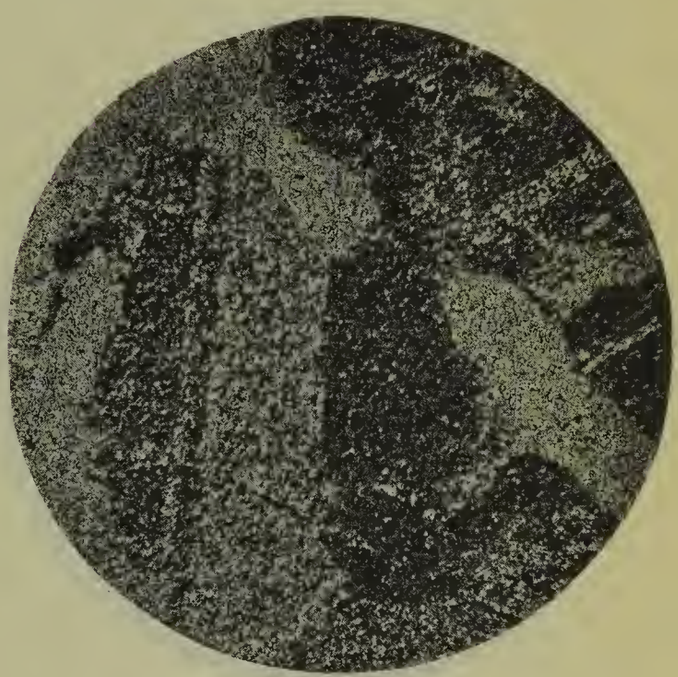
No. 11. "A" Silicon, Horizontal Section x 8.



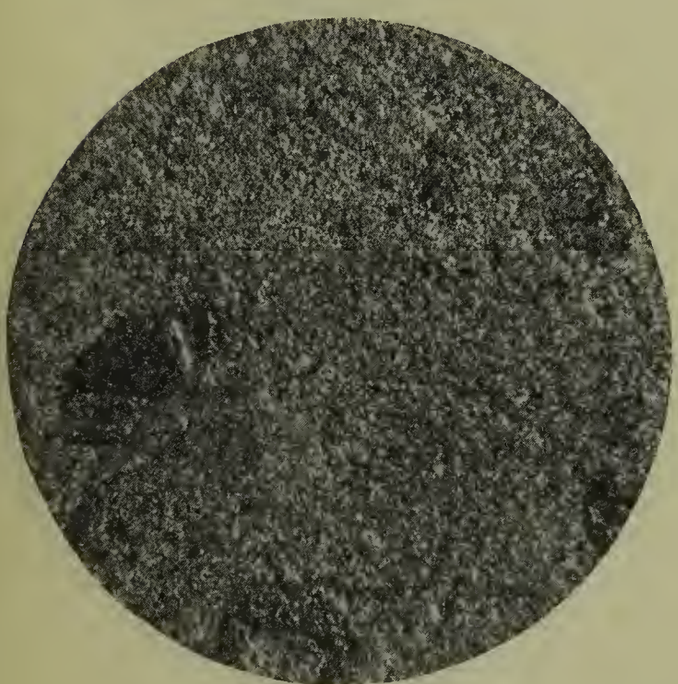
No. 12. "B" Silicon x 8.



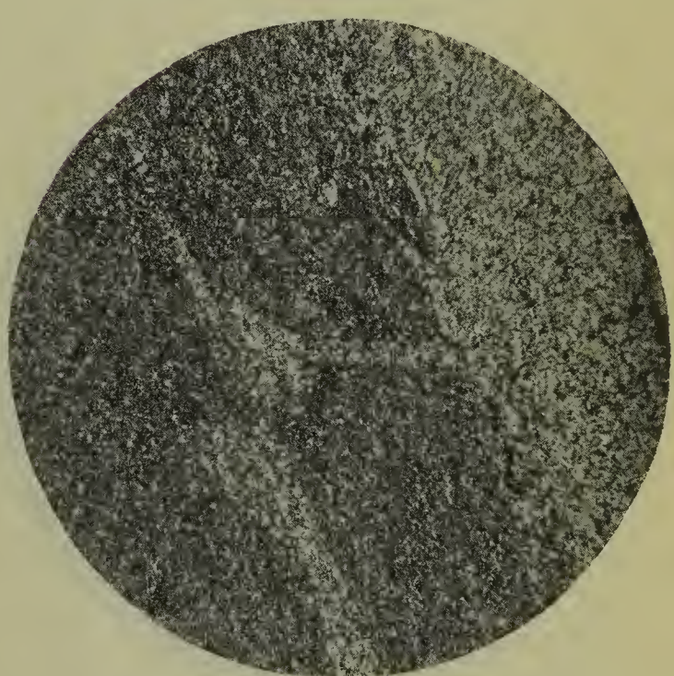
No. 13. "C" Silicon x 8.



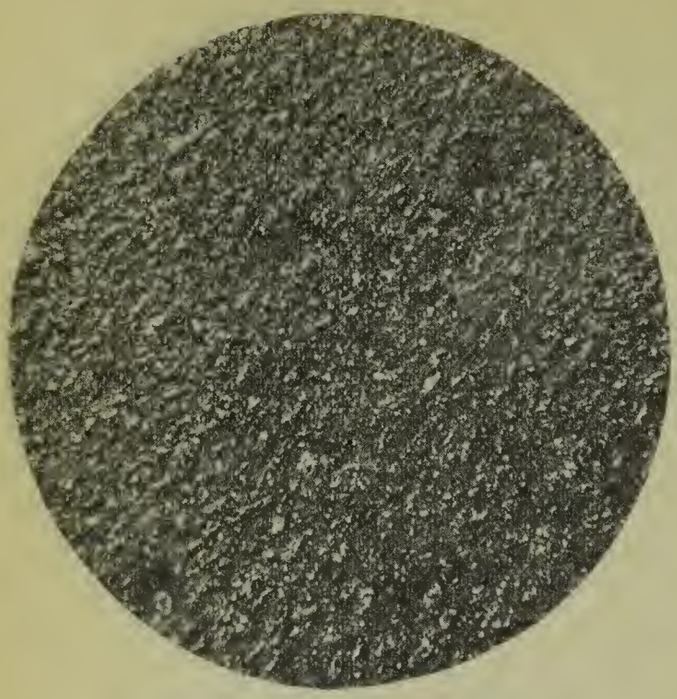
No. 14. "A" Silicon, x 34.



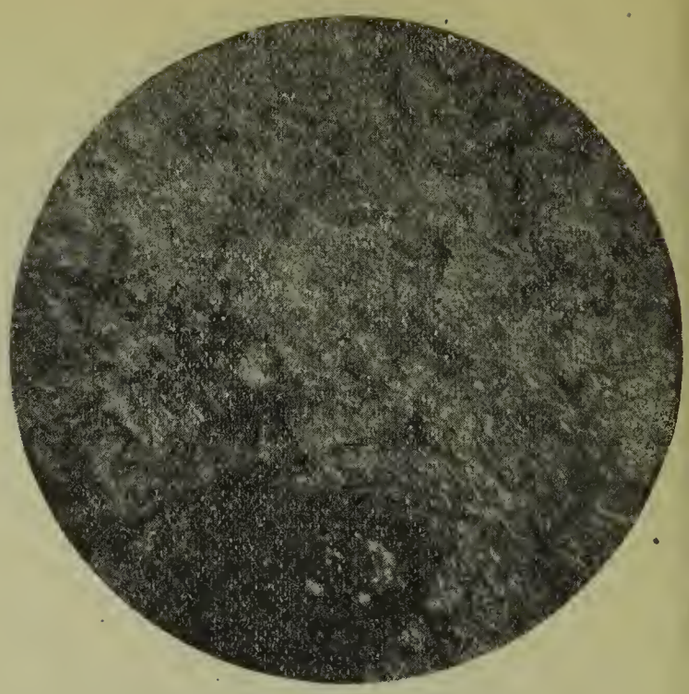
No. 15. "B" Silicon x 34.



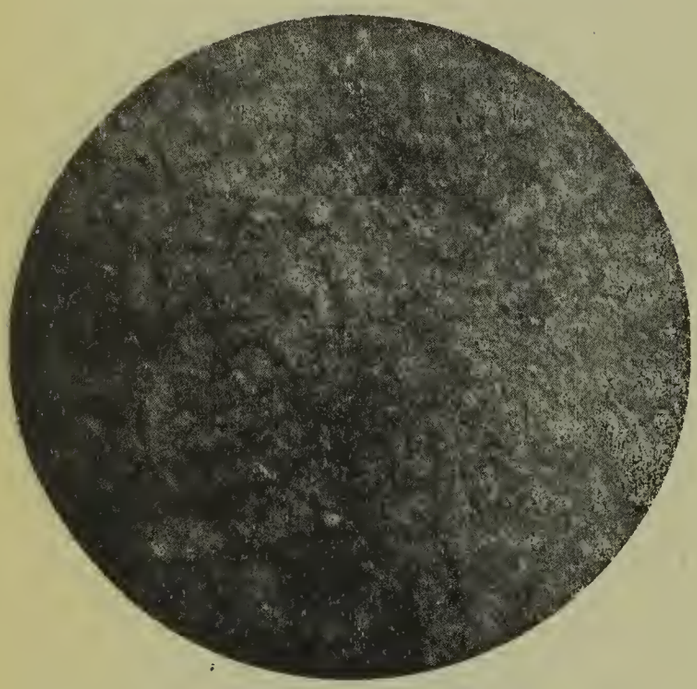
No. 16. "C" Silicon x 34.



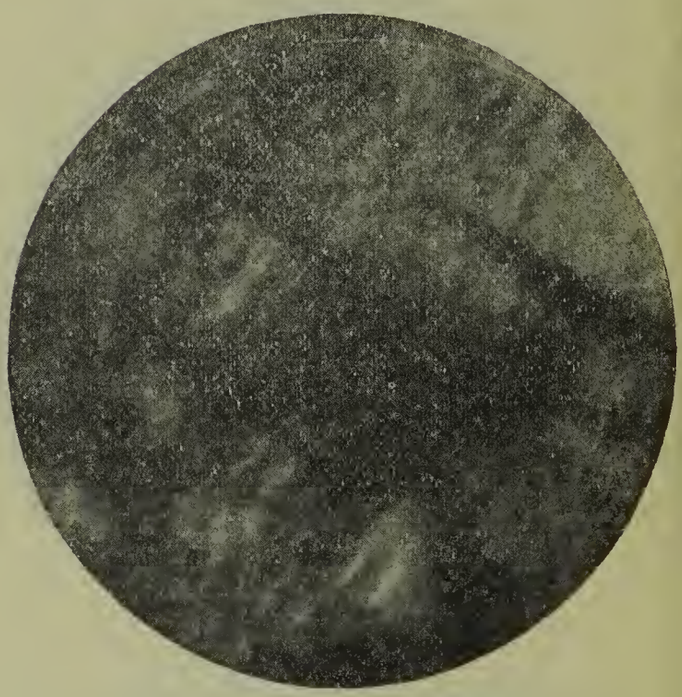
No. 17. "A" Silicon, v x 167.



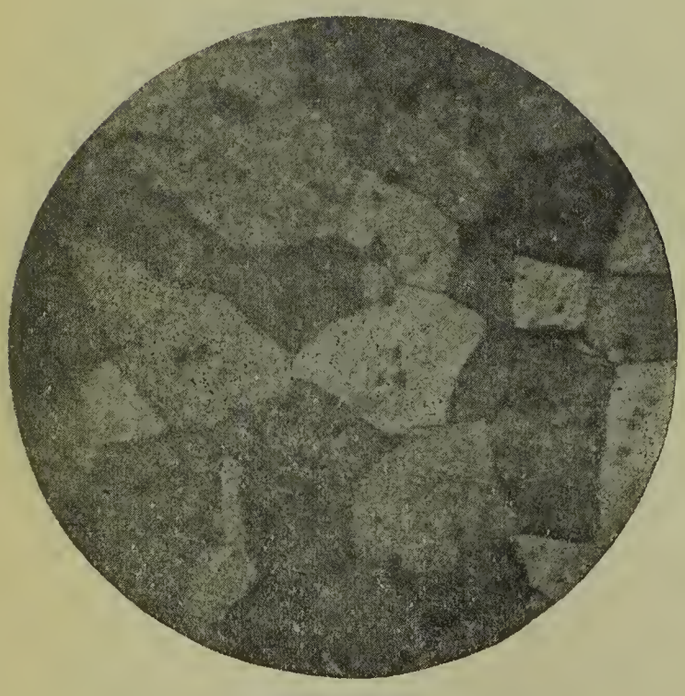
No. 18. "B" Silicon, v x 167.



No. 19. "C" Silicon, v x 167.



No. 20. "C" Silicon v x 1025.

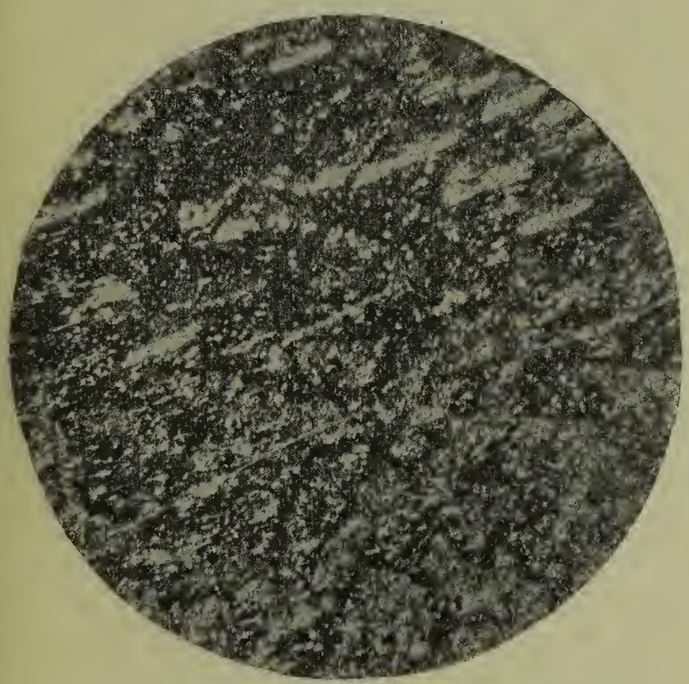


No. 21. Carbonless Iron v x 118.

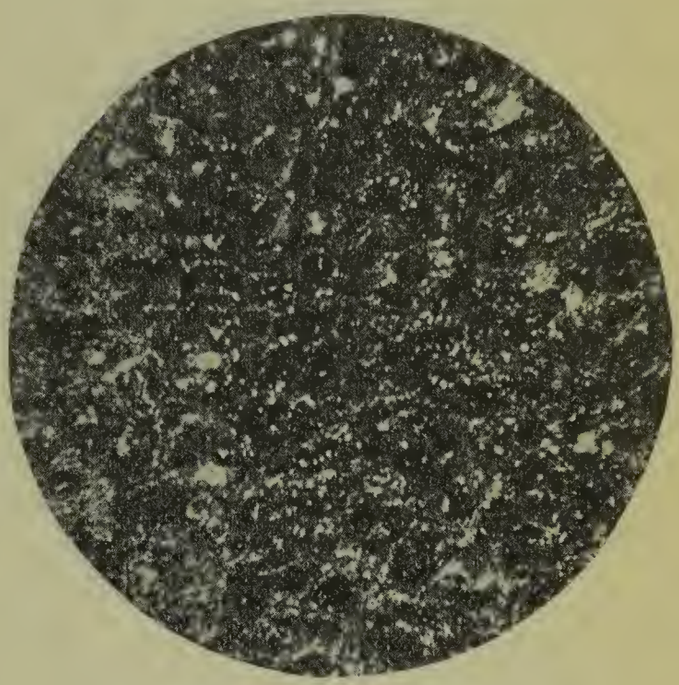
No. 22. 50% Ferro Silicon x 8.

No. 23. 52% Ferro Silicon x 8.

No. 24. 75%. Ferro Silicon x 8.

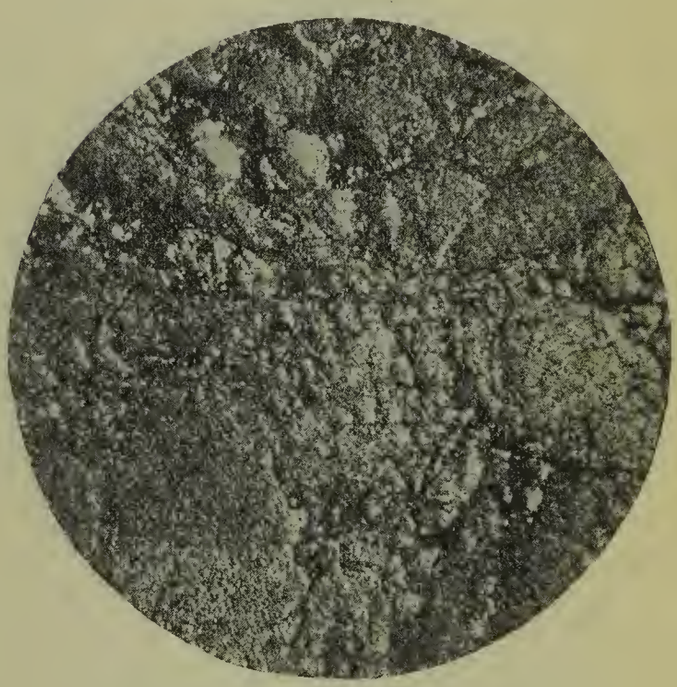


No. 25. 32% Ferro Silicon x 34.

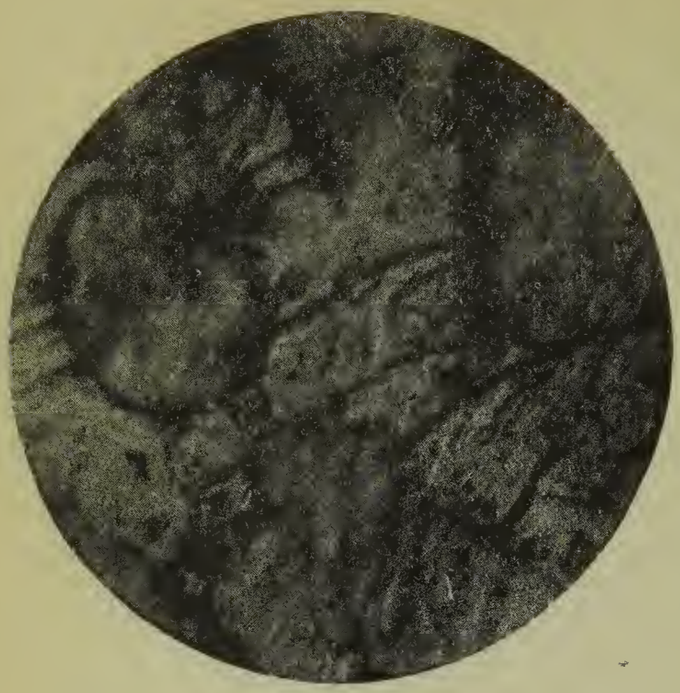


No. 26. 50% Ferro Silicon x 34.

No. 27. 52% Ferro Silicon x 34.

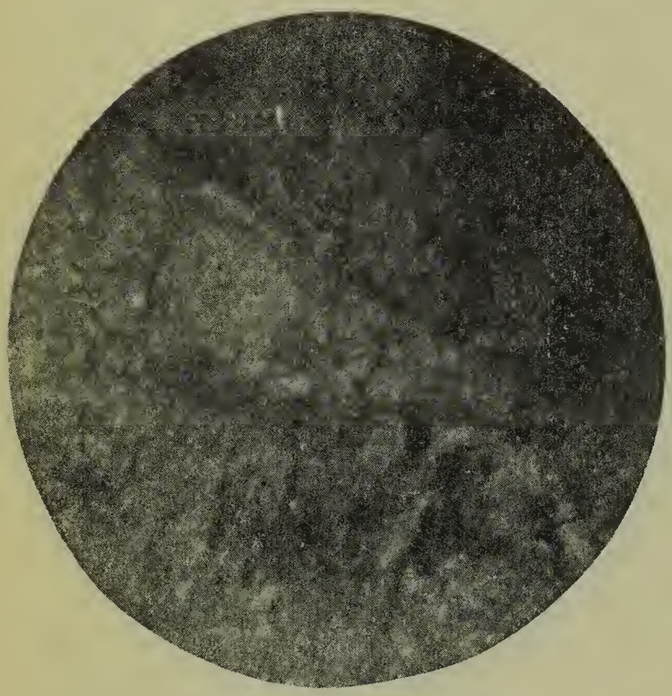


No. 28. 75% Ferro Silicon x 34.



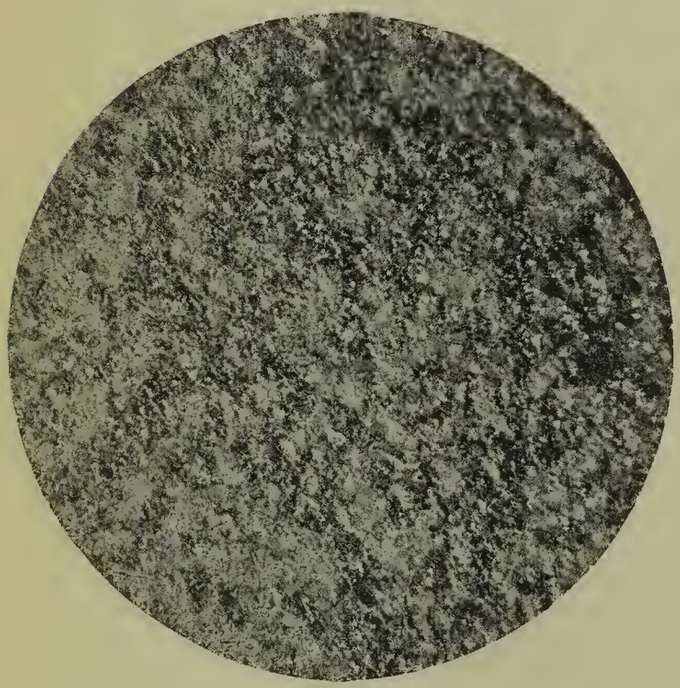
No. 29. 32% Ferro Silicon v x 167.

No. 30. 52% Ferro Silicon v x 167.

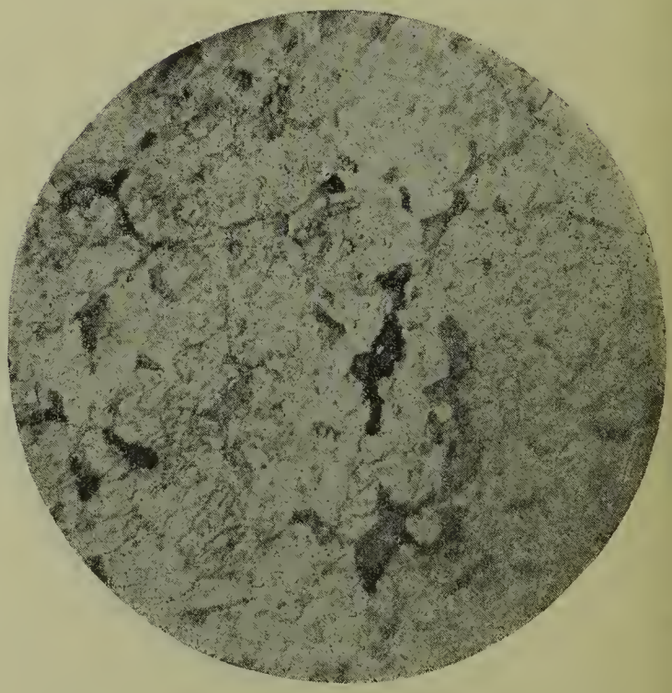


No. 31. 75% Ferro Silicon v x 167.

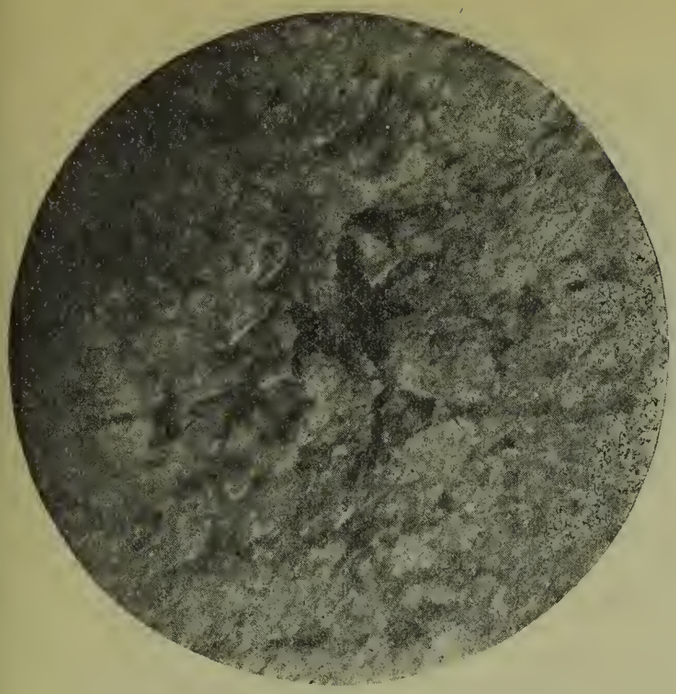
No. 32. S: 2.5%; cu. 97.7% x 34.



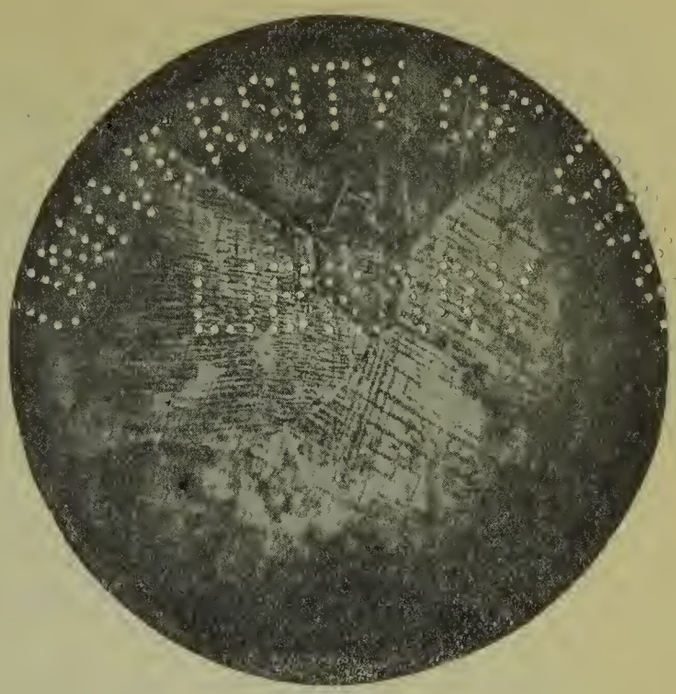
No. 33. 10.12%, S:; 87% Cu. x 34.



No. 34. S: 10.12%; Cu. 87.0% v x 167.



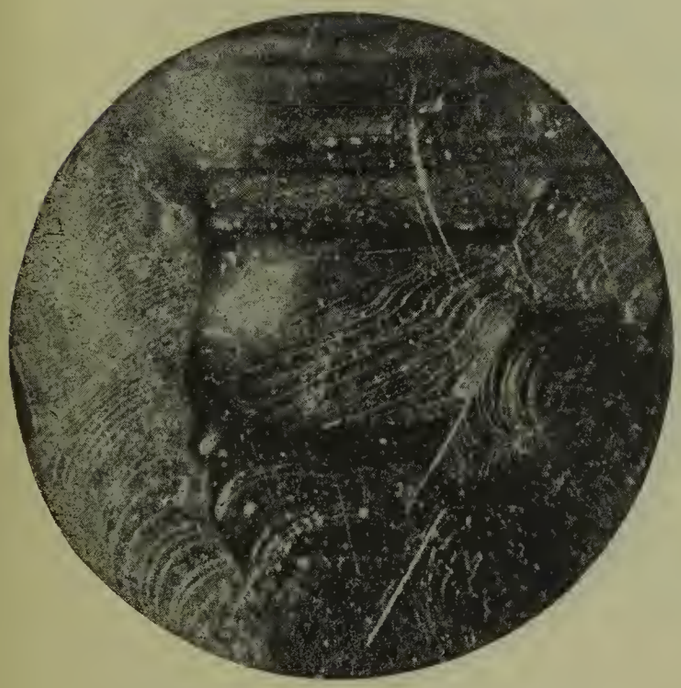
No. 35. S: 10.12%; Cu. 87.0% v x 167.



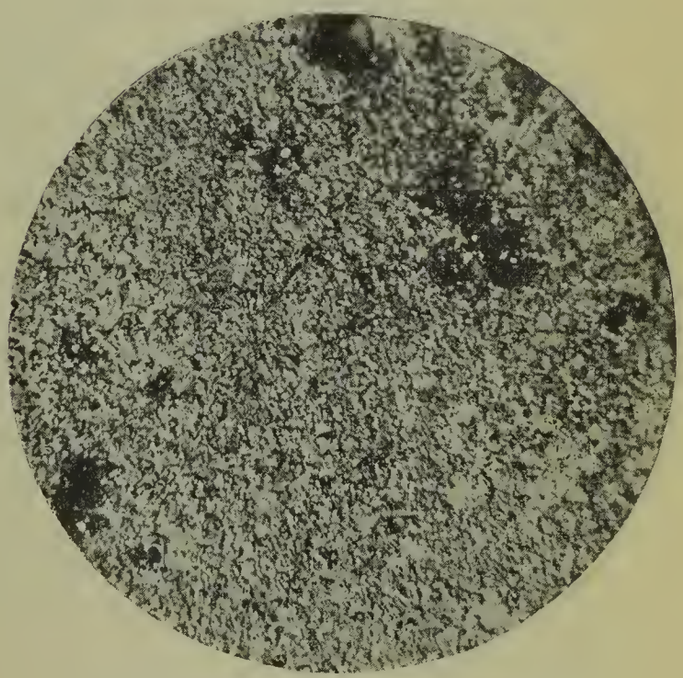
No. 36. 2.3% S:; 97.7% Cu. x 8.

No. 37. (See text) x 34.

No. 38. (See text) x 34.

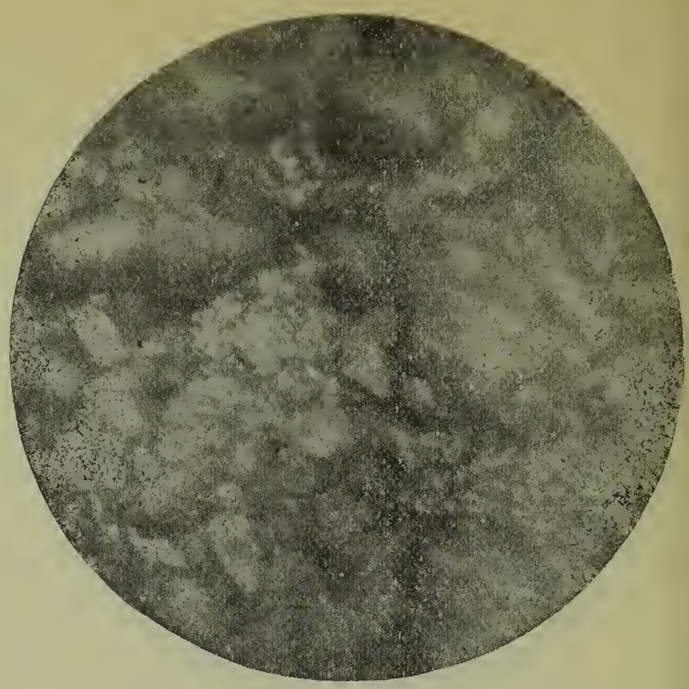


No. 39. S:c Crystals x 8.

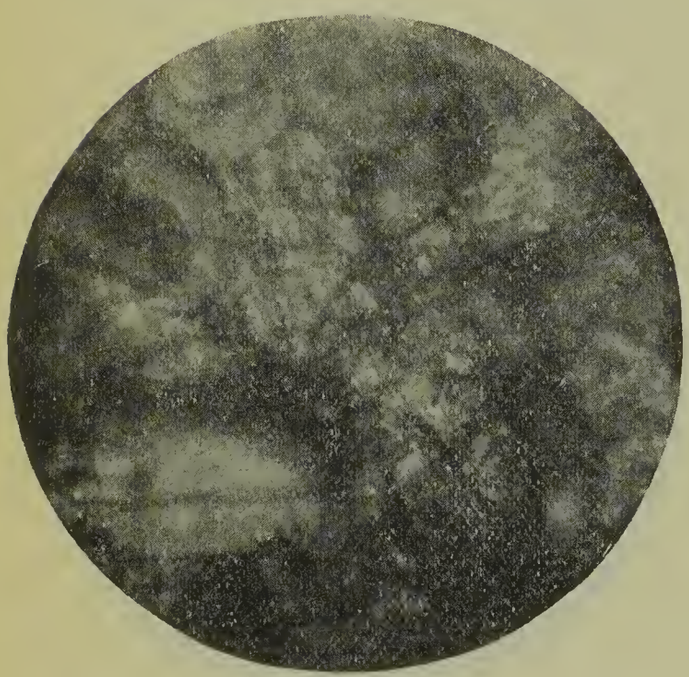


No. 40. 80% S:; 20% S:c x 8.

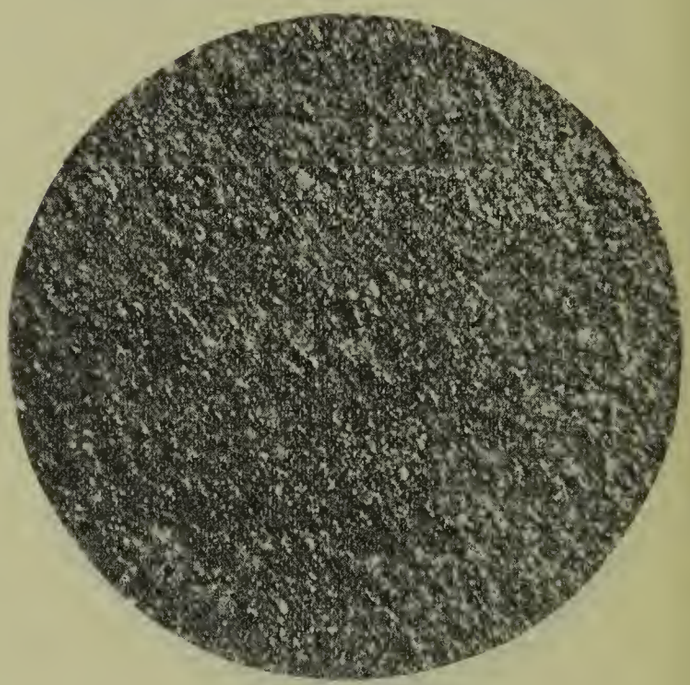
No. 41. 80% S: ; 20% S:c x 34.



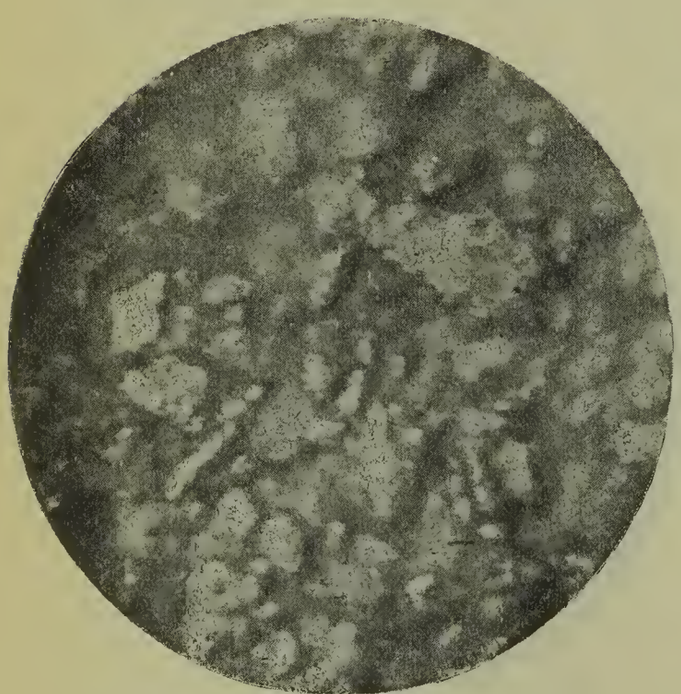
No. 42. 80% S: ; 20% S:c v x 167.



No. 43. 80% S: ; 20% S:c v x 167.



No. 44. Carbo Silicon x 34.



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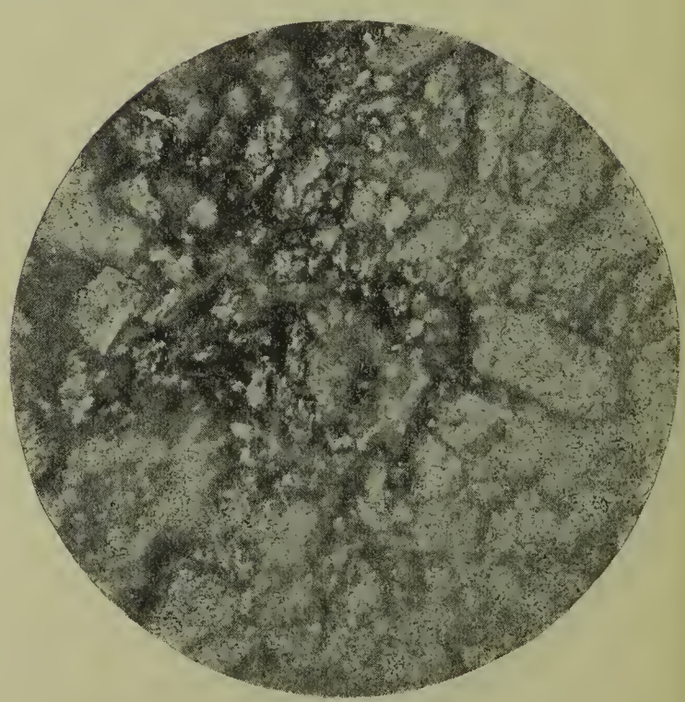

No. 46. Carbo Silicon, v x 167.

DISCUSSION.

PRESIDENT CARHART: I shall be obliged to ask the members of the Society to make their remarks on the paper as brief as possible on account of the shortness of the time that remains for the morning session. We have some other interesting things. Are there any remarks?

DR. H. R. CARVETH: I should like to ask the speaker if the specimens of ferrosilicon were annealed before the microphotographs were taken.

MR. ALBRO: Stead has shown that the structure of steel containing 4 per cent. of silicon is unaffected by heat treatment, and, as I have stated in this paper that the structure of silicon itself is unaffected by such treatment, it is fair to assume that the structure of the intermediate ferrosilicons is likewise unaffected.

DR. J. W. RICHARDS: I would like to call attention to the fact that the 50 per cent. alloy, which was shown, corresponds almost exactly with the formula $FeSi_2$. It is evidently a chemical compound of the iron and silicon. I think that the effect of this study may be to throw some light, possibly, upon the method of formation of these silicon carbon compounds, a question which I have myself studied a good deal, or thought a good deal about, such as the manner of formation of the silicon carbide, and I feel more convinced than ever that the volatility of silicon and the volatility of carbon at comparatively low temperatures has considerable to do with the formation of these compounds.

I cannot conceive of the method of formation of the silicon carbide crystals as they appear in the carborundum furnace when it is opened, except by the combination of silicon and carbon vapor to form the crystals *in situ;* because the crystals themselves are infusible. They decompose if heated, and yet they have been formed *in situ,* and I think they must have been formed from the silicon and carbon vapor.

PROF. FRANKLIN: I would like to know whether, in the increase of current due to an increase of voltage, the increased voltage does not show itself over what we ordinarily call the positive column, but not at the cathode?

DR. WEINTRAUB: Both vary.

DR. RICHARDS: The suggestion has come to me to ask

whether the fusible alloys of potassium and of sodium have been tried in the arc. It is the only other metal, I think, which is fusible at ordinary temperatures, and it resembles mercury.

Dr. E. Weintraub: I experimented with the potassium sodium alloy a good deal. An alloy containing about 6 per cent. of sodium is liquid at ordinary temperature and resembles mercury very much. With this material as a cathode I succeeded in making an arc in vacuo 10 inches long. The properties of this arc are very similar to those of the arc in mercury vapors. The light emitted is yellow reddish, and is mostly due to potassium, since potassium is much more volatile than sodium. This arc can be used in spectroscopic work, but as a practical illuminant it is not satisfactory for two reasons: First, because the efficiency is very low, and second, because the vapors of the alkali metals attack the glass with formation of silicon and other black substances, which cover the glass and soon cut off most of the light emitted.

Dr. Richards: One other question (if I may ask it, Mr. Chairman)—whether it would be possible, when using an alternating current, to use an aluminum rectifier cell to start it.

Dr. Weintraub: It is not necessary to use direct current to start the rectifier. A small additional electrode of mercury is used, which is very close to the cathode, and is connected to one of the terminals of the alternating current. By a slight tilting of the tube a little spark is produced between the cathode and the auxiliary electrode, which starts up the rectifier. If, however, the rectifier is used to charge a storage battery, the battery itself can be used to supply the starting direct current arc.

A paper read at the Seventh General Meeting of the American Electrochemical Society, held at Boston, Mass., April 27, 1905. President Carhart in the chair.

THE MERCURY ARC.

By E. Weintraub, Ph.D.

INTRODUCTION.

This paper contains results of an investigation on the properties and nature of the conductivity of metallic vapors carried out in the Research Laboratory of the General Electric Company. The investigation was started with the practical purpose in view of using the arc discharge in metallic vapors, and especially mercury vapors, as a source of light. The principal practical problems to be solved at the time when I began the investigation (about four years ago) were as follows:

1. The starting of the discharge in metallic vapors in an instantaneous and automatic way by the current itself.

2. The determination of conditions under which an alternating voltage can be made to maintain an arc in metallic vapors.

3. Determination of the factors influencing the stability of the arc, with the purpose of constructing a lamp stable under varying external conditions.

4. The production of an arc of the character named which would emit rays belonging to different spectral regions in such proportions as to constitute white light.

None of these problems could be solved on the basis of the knowledge then available, and pure theoretical investigations had to precede any attempt of their solution. Each one of these problems will be taken up separately, and particular emphasis will be laid on the results of theoretical importance. The general problem of conductivity is one of the most important in science, treating as it does of the relation between matter and electricity. The subject is of special interest to the electrochemist, whose science can be in the main properly defined as the science of conductivity of a particular kind of matter, namely, of solutions and molten salts. The ionic theory of conductivity that had its

birth in electrochemistry found afterwards fruitful applications in the theories of conductivity in gases. Any increase of our knowledge in this last named branch is in its turn apt to react on the general structure of that theory, and eventually influence the electrochemical ideas themselves.

§1. STARTING OF AN ARC IN METALLIC VAPORS.

(a) The role of the cathode in the starting process.

The distinctive feature of the conductivity of gases and metallic vapors, in contradistinction to that of metals and electrolytes, consists in that under ordinary conditions, in absence of exterior ionizing agents, *the current itself has to create the material which is to carry it from one electrode to the other.* As this material does not exist at the beginning, some special means must be used to *start* the discharge, and thus we meet in gases and vapors with the problem of starting, a problem unknown in the realm of conduction through metals and electrolytes. If, to take the particular case which interests us here, a glass tube having two mercury electrodes, and exhausted, is connected to a source of moderate electromotive force, no current passes, no matter whether the tube is cold or filled with mercury. Two different ways were used to start the arc discharge. The first one consists in bringing the two electrodes into contact and then separating them. This method is exactly the same as the one used in the carbon arc, the flame arc, etc. The second one is founded on the use of a high voltage shock. The Geissler discharge through the residual gas or mercury vapor in the tube creates a conductive path, the moderate direct current voltage follows and the arc discharge is initiated. Both methods were used by the investigators of the mercury arc, especially by Arons, in Germany, and Cooper Hewitt in this country.

The new way of starting an arc discharge in mercury vapor that I want to expound here was the outcome of the theoretical conceptions on the mechanism of the arc and the function of the ionization at the cathode surface that I formed in the course of these investigations. According to these conceptions, an arc discharge in metallic vapors is a *discharge deriving its carriers, at least in the immediate neighborhood of the cathode, from the*

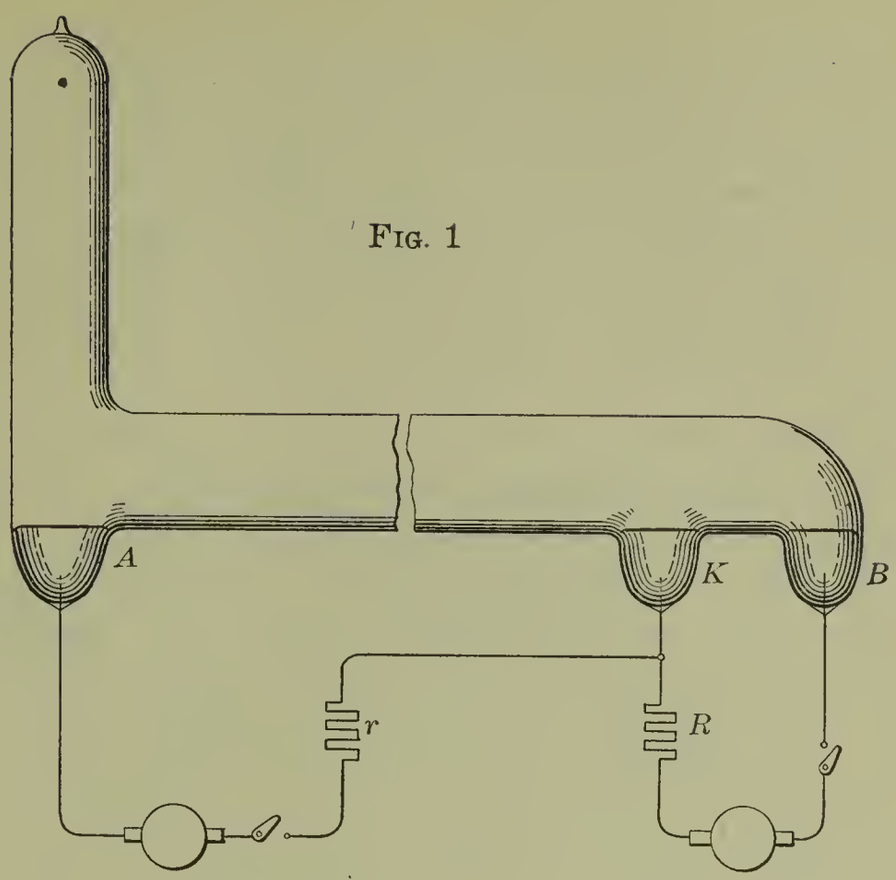

Fig. 1

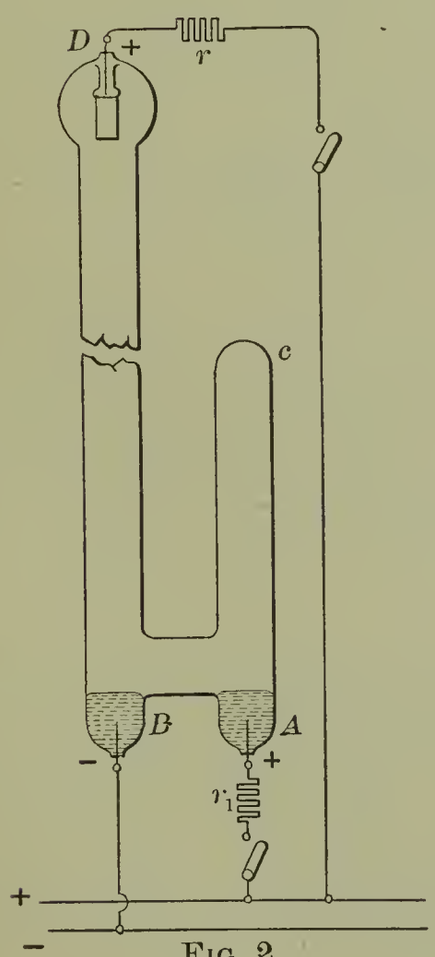

Fig. 2

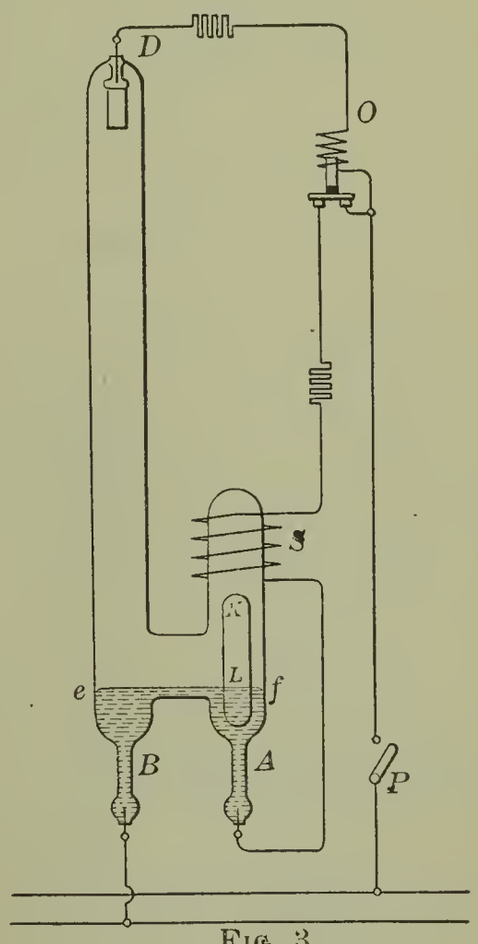

Fig. 3

material of that cathode. The application of a moderate electromotive force is of itself insufficient to start the process by which these carriers are formed out of the material of the cathode. The new fact discovered was that this formation of carriers (the "ionization" process) is started and the arc discharge made possible *if a spark or a small arc is produced at the surface of the cathode.* The following experiment will serve to illustrate this statement:

The tube is represented in Fig. I. K is a cup filled with mercury. A and B are electrodes of graphite, iron or mercury. In the figure they are shown as mercury cups. The tube is exhausted on the Sprengel pump to the highest possible vacuum, and by some means, such as heating from outside, or by the arc itself, the gases are driven off from the walls of the tube and the anode material. Two different sources of direct current are used, one applied to K and B, the other to K and A, in such a way that K is the negative pole of both. If, now, the *little arc BK is started by bringing the electrodes into contact and separating them, the other arc, K A, starts instantaneously.* If the connections are changed in such a way that K is the common positive pole of the two sources, the arc BK does not cause the starting of the arc AK. The fundamental importance of the cathode in the process of starting an arc is illustrated by this experiment in a simple and striking way. We can dispense in the tube of Fig. I with the use of two different sources and use the same source with different resistances in the two branches. In Fig. II, B is the cathode, D and A are both connected to the positive pole; r is a large resistance; r_1 is a small resistance used for the purpose of regulating the current in the main arc BD. By slightly shaking the tube, the arc BA starts, whereupon the arc BD starts of itself. The switch in the side branch arc BA can then be opened and the auxiliary arc discontinued.

For the practical use of this starting method the operations of separating the electrodes B and A and discontinuing the auxiliary arc the moment the main arc is started must be performed automatically by the current itself. One of the arrangements that I have devised is represented in Fig. III. KL is an iron plunger, S a solenoid and O a magnetic cut-out. The solenoid S, in pulling up the plunger KL, produces the auxiliary arc. The

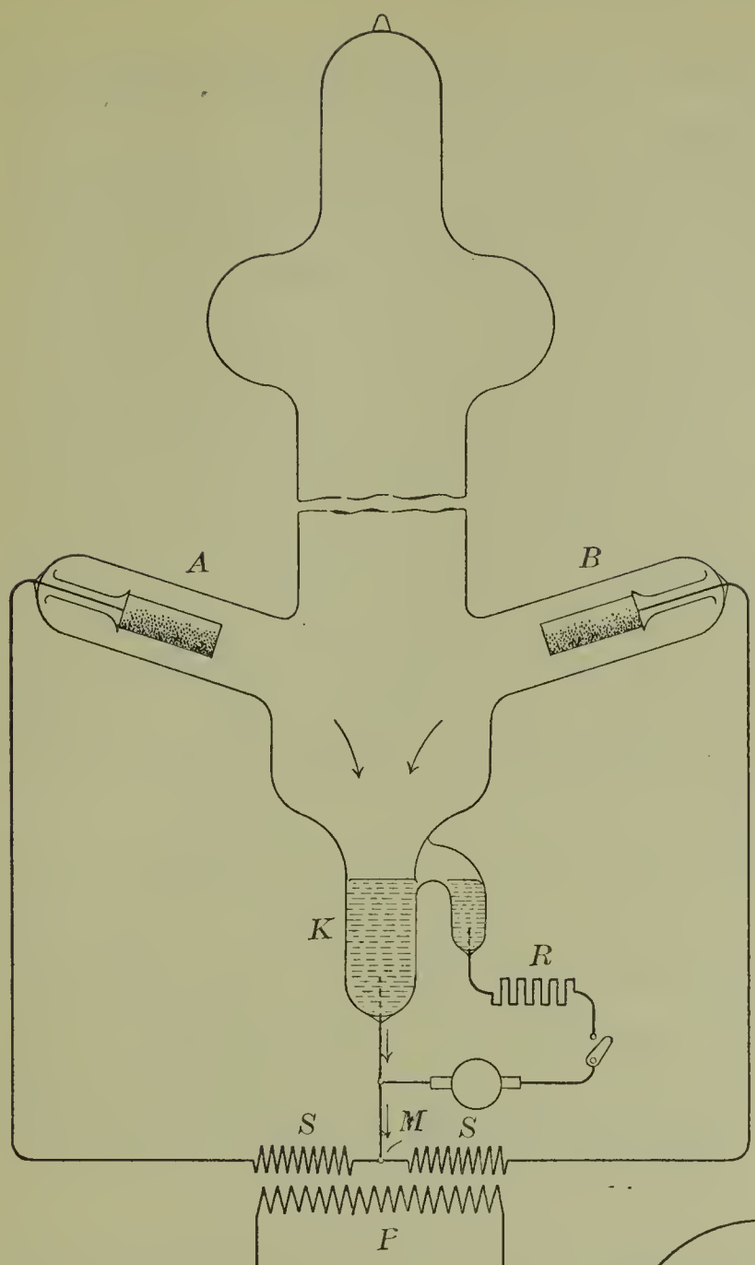

FIG. 4

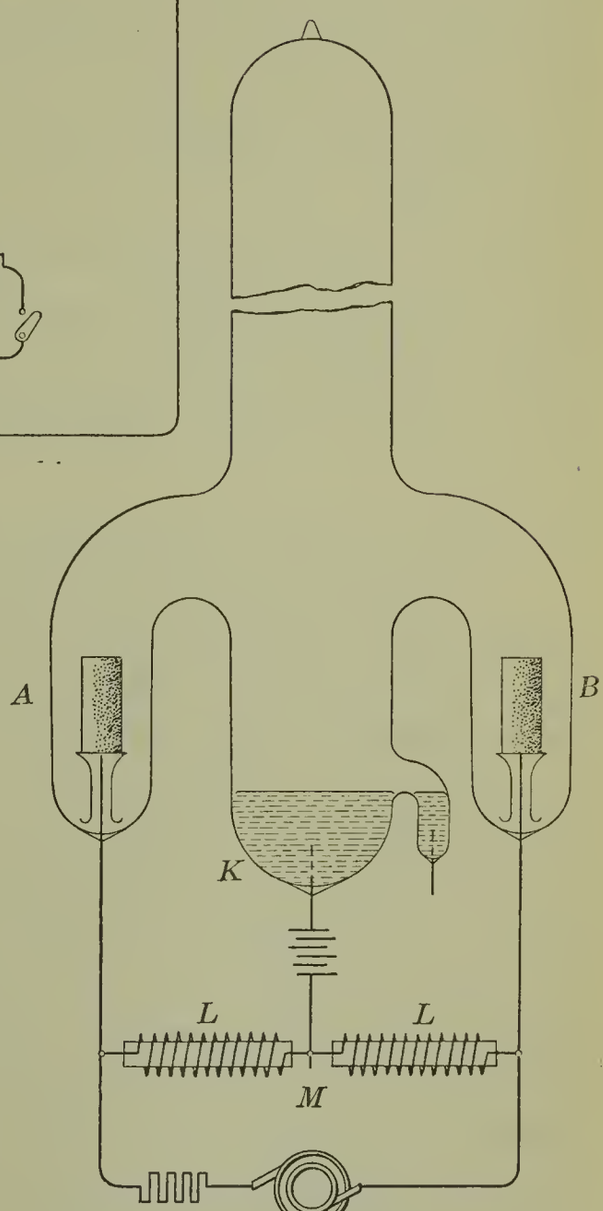

FIG. 5

current in the main arc flows through the magnetic cut-out and automatically opens the circuit of the auxiliary arc.

It is interesting to remark that the old method of starting an arc by contact is based also on excitation of the cathode; only, instead of having one arc instantaneously formed by another, we have a continuous growth, a short arc producing a longer one.

As a development of the old contact method I have used the following way, which is based on the use of a carbon filament of high resistance, which first establishes connections between the anode and cathode, so that on closing the switch the current first flows through the filament. By means of a solenoid and its magnetic action on an iron plunger the filament is lifted and the contact between its lower end and the mercury cathode broken. Exactly as in the case of the old form of contact method the small arc lengthens until the carbon filament is short-circuited by the arc.

I shall not attempt the description of all the schemes and arrangements used. I myself devised a number of them, and Steinmetz, Whitney, Wood and other members of our laboratory have invented a number of ingenious ways of producing the same result. A series of different types of lamps have thus been developed. They are all founded on the principle of the excitation of the cathode and differ merely in mechanical details.

(b) Influence of the conditions prevailing in the space between the electrodes on the starting process.

The space separating the electrodes has an important influence on the velocity with which the starting takes place, but this influence is mainly of a negative character. The space *must present as little hindrance as possible to the flow of ions starting from the cathode surface.* Accordingly, the degree of vacuum must be the highest obtainable, and the more careful the exhaustion the more instantaneous is the starting. If foreign gases, or inert ordinary mercury vapor, are present, the starting is slow. The ionized vapor is seen to rise from the surface of the cathode and slowly move along the tube, impeded in its motion not only by the gases present in the tube, but also by the mercury vapor which volatilizes from the heated surface of the mercury cathode. When the vapor reaches the

anode the arc will eventually start, but if the pressure of the foreign gases is high enough the arc does not establish itself at all. Although it is relatively easy to produce the high vacuum necessary for the instantaneous starting, it is not easy to drive out completely the gases absorbed on the walls of the tube and in the anode material. The vacuum in the lamps is liable, in some cases, to get worse with use, and some means had to be provided which would render the starting of the arc instantaneous, even with a somewhat impaired vacuum (pressure of foreign gases above .01 mm.). As inert mercury vapor also hinders the propagation of the ionized vapor, even perfectly exhausted lamps start harder when hot than when cold. I found that the propagation of ions and the starting of the arc are facilitated if a carbon filament of high resistance is suspended from the anode in such a way that its lower end is distant but a few inches from the mercury surface. When the ionic stream reaches the lower end of the filament a small current is established which helps the starting of the main arc.

(c) Function of the anode in the starting process.

In contradistinction to the cathode the anode plays no rôle whatever in the starting process. It receives the carriers of the current without any previous excitation.

§2. CONDITIONS OF STABILITY OF THE ARC.

(a) The influence of the conditions at the cathode surface.

In the study of the conditions of the stability of the mercury arc one meets with a phenomenon which is being observed in all arcs, *i. e.*, the existence at each impressed voltage of a lower limit of current, below which the arc is not stable and extinguishes. The experiments performed on the mercury arc led me to the conclusion that *the physical cause of it is in the conditions prevailing at the very surface of the cathode.* Under ordinary circumstances there is a bright spot on the surface of the mercury cathode, which spot is continually wandering about on that surface. The wandering of this spot has not found as yet any very satisfactory explanation. This spot is, according to the conceptions expounded here, the place where the production of ions takes place, and the continuous motion of that spot means a dis-

turbance of the ionization process and a danger to the existence of the arc. The wandering of the spot can be avoided in two different ways: either by making the surface of the cathode small, of the same magnitude as that of the spot, or by having a wire of iron or platinum project above the surface of the mercury. In this latter case the cathode spot is centered on the mercury surface right around the metallic wire. In order to limit the surface of the cathode, without changing anything else in the tube, narrow tubes of refractory material, such as silica or porcelain, are fastened inside of the mercury cathode. The arc is started by means of a carbon filament which dips into that small tube. The filament is lifted by the passage of the current, the current broken and the little spark produced inside of the narrow tube. This spark causes the main arc to start with its cathode inside the narrow tube. The rest of the mercury surface outside of the small tube is then inert and does not carry any current. This is, by the way, an experiment showing strikingly that the arc has its root in the cathode spot.

Both methods lead to the same result, the lowering of the minimum current at which the arc subsists. With 120 volts applied and about 80 volts consumed by the arc, the lower limit of current is normally at about 3 amperes. When the cathode surface is made very small this limit decreases to 1.5 amperes, and with a platinum wire it becomes as low as 1 ampere. These values can be made much smaller if reactance is placed in the circuit or if the impressed voltage is higher.

(b) Influence of the conditions prevailing in the space between the electrodes on the stability of the arc.

The conductivity of the arc depends on the relative amounts of ionized and inert mercury vapor. If a sufficient condensing space is provided, so that the pressure of the ordinary mercury vapor volatilized from the cathode is kept down to a certain value, *the conductivity of the arc is almost exactly proportional to the current.* (The current creates its own ions; Ohm's Law is *not* applicable.) The voltage across the arc is accordingly almost independent of the current. If, however, sufficient condensing space is not provided the amount of inert mercury vapor rises continually, and with it the resistance of and voltage across the arc,

until finally, when the voltage across the arc comes too near to the impressed voltage, the arc goes out. Foreign gases present in the tube have influence similar to, and even more pronounced than that of mercury vapor.

The statements above give a complete description of the influence of the conditions prevailing in the arc itself on its stability. They have no noticeable effect on the value of the lower limit of current.

(c) Influence of the conditions at the anode.

The conditions prevailing at the surface of the anode have no appreciable effect on the stability of the arc. If the anode is made of mercury, great amounts of mercury vaporize because of the heat generated at the anode. This increases the amount of mercury vapor in the arc, and thus indirectly changes the conditions of stability of the latter. This is obviously a secondary effect; otherwise, the anode has just as little effect on the stability of the arc as it has on the starting process.

§3. THE ALTERNATING CURRENT ARC IN METALLIC VAPORS.

We have seen in the preceding chapters that the ionization process at the cathode must be initiated if an arc discharge in metallic vapors is to be established, and that this ionization process must be kept up by the supply of a certain amount of energy if the arc is to maintain itself. It is in these facts that lies the explanation of the difficulty that previous investigators have found in maintaining an alternating current arc between metallic vapors. With every change of polarity the ionization process at the cathode dies out and moderate electromotive forces are insufficient to start that process by themselves on the surface of the other electrode when the latter becomes of negative sign. It is therefore obvious that if an alternating electromotive force of moderate value is to maintain an arc in metallic vapors, one metallic electrode must permanently keep its negative sign, notwithstanding the perpetual change of polarity. This, if realized, would mean a unidirectional flow of current in the arc, and consequently rectification of the alternating current.

If, referring to Fig. I, the electrodes K and B are connected to a source of direct current, K being the cathode, and a source

of alternating electromotive force is applied to K and A, that half of the alternating current which has the direction AK (K cathode) passes, since the ionization process at the surface K is kept up by the direct current arc; the opposite half wave is completely suppressed. The arrangements by means of which both halves of the current wave are made to pass in the arc and are superposed in the same wire are mainly applications of electrical principles to the given case. Of all the devices used by me I will mention but two. In both of them the tube contains three electrodes, one of mercury, the others of graphite, iron or mercury. The one electrode of mercury serves as the cathode, the two others, which we will suppose to be made of graphite, serve as anodes of the rectified arcs. In the first arrangement, represented on Fig. 4, a transformer is used, the ends of the secondary of which are connected to the two graphite anodes. A wire taken out from the middle of the secondary is connected to the cathode. One half wave takes then in the arc the direction AK, the other the direction BK, and both are superposed in the same direction in the neutral wire of the transformer. The current derived is pulsating, and if the rectified voltage or current is low, usually a small direct current arc, springing from the same cathode, is necessary to keep the cathode alive during the zero point of the current. If a constant current transformer is used this direct current arc can be dispensed with.

In the second method the alternating voltage is directly applied to the two graphite electrodes and two reactance coils are connected in the way shown in the figure (5). As in the first arrangement, two arcs are playing in the tube, both having the same cathode. The reactances store up energy, while the current flowing in them increases and discharge through the arc in such a direction as to keep the cathode K alive. In this case, as in that of the starting method, described in the first chapter, a great number of modifications and combinations have been devised, both for monophase and polyphase currents, the description of which would add nothing of theoretical interest. By means of arrangements of this kind I succeeded in rectifying voltages up to 15,000, giving direct current voltage as high as 6,000 to 7,000 volts. This last arrangement may become of importance, even for laboratory use, when unidirectional high voltage is desired.

One phenomenon is being observed in the mercury arc rectifier

which is of theoretical importance. As is seen from the figure, the alternating voltage is applied directly to two electrodes, which, when the rectifier is working, are surrounded by a highly conducting vapor. Without the knowledge of the cathode properties and the necessity of creating an ionization center on its surface, the fact that no short circuit takes place would be incomprehensible. Under certain conditions, however, this short circuit takes place, one of the two electrodes becoming the cathode of an arc discharge. This phenomenon is termed "arcing" of the rectifier. There is no doubt that under normal conditions a small leakage current flows between the two anodes of the rectifier. A number of experiments have shown that if an electromotive force is applied to two exploring electrodes placed in the mercury arc a slight leakage current of the magnitude of 1 milli-ampere flows between those electrodes.* The question of arcing is accordingly identical with the following one: Given two electrodes, separated by a highly ionized vapor and an electromotive force applied to them, under what conditions will a cathodic center form and the small leakage current transform into an arc discharge. By a series of experiments a number of factors influencing the arcing have been determined, so that rectification could be carried up to many thousand volts A. C., with practically no arcing at all. It would lead me too far to treat this difficult question here. One point of theoretical interest will be mentioned later on in connection with the question of the nature of the ionization process at the cathode.

§4. ARC DISCHARGE IN VAPORS OF ALKALI METALS.

With the purpose of adding red lines to the spectrum of the mercury arc I investigated the arc discharge in vapors of other more or less volatile metals. Alkali metals proved especially suitable. The experiments showed that the *regularities found during the study of the discharge in mercury vapors hold good for all other metallic vapors.* The cathode phenomena, the bright cathode spot, the behavior toward alternating voltage are exactly the same. Accordingly, all of the experimental facts established in the previous chapters hold good for the discharge in metallic vapors in general.

* The experiments have shown that this leakage current is exactly proportional to the current in the arc. It is to this kind of conductivity that we probably owe the possibility of measuring the potential between two exploring electrodes sealed into the path of the arc by means of an ordinary current-using voltmeter.

§5. ON THE MECHANISM OF THE IONIZATION PROCESS AT THE CATHODE.

In the preceding paragraphs the important rôle of the processes taking place at the cathode surface has been experimentally proven. An insight into the mechanism of these processes would give us a basis to the theory of the arc discharge, and of the conductivity of gases in general. The first question I tried to answer by experiments was, whether the ionization process at the cathode is accompanied by an actual transfer of matter or not. The attempt of previous workers on arcs to answer this question in case of the open-air arcs was unsuccessful. The mercury arc presents a better opportunity for the study of this question, since the arc takes place in a vacuum and the mercury undergoes no chemical change. Unfortunately, the phenomenon is complicated by the volatilization of mercury, due to the heat generated at the electrodes. If two mercury electrodes are used the mercury actually distills over from the anode to the cathode, the amount of heat generated at the anode being greater than that generated at the cathode. To simplify conditions a graphite anode was used in all the experiments. In this case the mercury distills over in great quantities from the cathode into the condensing space surrounding the anode. This mercury is, however, in the greatest part produced by mere volatilization of the cathode. If the mercury cathode is cooled artificially, so that the heat generated is conducted rapidly away, the amount of the condensed mercury diminishes considerably, and if the wandering of the cathode spot is avoided by the projecting wire method this amount is still further diminished. The amount of mercury that condenses under these conditions in the condensing chamber surrounding the anode is very small and constitutes but a small part of the amount required by Faraday's Law. The largest part of it is, however, still due to mere volatilization which cannot be completely avoided.

An attempt was made to get quantitative data by using mercury arcs with cathodes made of less volatile material than mercury. If a piece of graphite or any other conducting material that does not combine with mercury, and a mercury cup, both enclosed in an exhausted tube, are connected to respectively the negative and positive pole of a source of an electromotive force, the elec-

trodes brought into electrical contact and separated, an arc is formed with the solid electrode as cathode. The behavior of these solid cathodes is the same as that of the mercury cathode. A bright spot is wandering on the surface of the solid piece and wherever that spot strikes the cathode disintegration of its material takes place. *This disintegration is characteristic of the cathode of a metallic arc in an exhausted space.* If a piece of charcoal is used as a cathode the motion of the cathode spot leaves fine lines and grooves burned, so to say, into the material. The loss of weight of these solid cathodes is usually very small. The largest part of it is, however, due to the mechanical disintegration of the material which accompanies the electrical one, which circumstance deprives the results of theoretical significance. *We can, therefore, conclude from these experiments that a transfer of matter either does not take place at all, or is so small as to be of the order of magnitude that would be required by the value of the electronic mass accepted in the modern theories.*

The second question of special interest in connection with the theory of the arc refers to the *cause* of the ionization process at the cathode. The formation of current-bearing particles does not in all probability take place at all in the arc itself. The potential drop in the arc and that at the cathode surface (about 5 volts) are so small that productions of ions by collision seems to be excluded. As the anode plays no appreciable rôle during the starting and the running of the arc we are led to the conclusion *that in an arc through metallic vapors in an exhausted space the cathode is the only place where the current-bearing material is formed.*

The assumption that the cathode is *one of the places* where ionization takes place has been made by many previous investigators. In view of the fact that solid bodies heated to a high temperature are known to render gases conductive (effect that I observed myself in the case of mercury vapor), the ionization process at the cathode was attributed by some of the investigators to the high temperature prevailing at the cathode. The experience that I have had on arcs in metallic vapors, and special experiments made to elucidate this point, do not support this view. The boiling point of mercury being low, it is necessary, of course, to limit the supposed area of high temperature to the cathode spot itself.

The facts that speak against this assumption are as follows: First. As mentioned above, the cathode spot moves rapidly along the surface of the cathode. If high temperature were a necessary condition of the ionization process the cathode spot would not be expected to move constantly away from the exceedingly hot part to the cold part of the surface. Second. If the spot is fixed by means of a platinum wire no evidence of a high temperature in that spot can be found. The faint light emitted by the spot surrounding the wire reminds one, especially when the current is not very high, rather of a phosphorescent light than of light produced by high temperature. Third. Efficient cooling of the cathode does not produce any change, either in the cathode spot or in the arc. To cool the cathode efficiently I used the following method:

A platinum cap, sealed into glass, is connected to the negative pole and a surface of mercury to the positive. By heating the mercury some of it was made to condense on the platinum cap, so that this thin layer of condensed mercury could be used as a cathode. The cap was cooled by rapidly flowing water. The arc showed no difference in its behavior, with the exception that the cathode spot wandered about with an extraordinary velocity along the mercury layer. In this case one can still claim that some infinitesimally small point of that layer has at any moment an exceedingly high temperature. One will, however, admit that this assumption is not a very probable one.

Fourth. If solid cathodes, such as graphite, iron, platinum, etc., are used, the cathode spot on the surface, to judge by its color, has not a very high temperature, so that the rapid disintegration is not due to volatilization by heat, but rather to purely electrical causes. If, by an auxiliary current, the solid cathode is heated up in such a way that one part of it, by reason of its higher resistance, is brought to a very high temperature, the cathode spot wanders about the surface of the cathode without showing any preference for the hot spot, which would be expected if high temperature were the cause of ionization.

Fifth. In the case of an "arcing" rectifier, where we have to deal with the *formation* of the cathode spot, *temperature* of the solid electrodes plays but an unimportant rôle. The electrodes may be very hot while surrounded by ionized vapor without

causing arcing. This is very significant if compared with the relative ease with which at first sight seemingly unimportant factors produce arcing. If, for instance, the electrodes are of mercury, a drop of mercury hitting the surface, or any other mechanical disturbance, is liable to produce a cathode at the point where impact takes place. These and a number of other facts, for which I have not space here, led me to the conclusion that the *temperature of the cathode is not the cause of ionization in the case of metallic arcs in an exhausted space.* The temperature of the cathode is probably in some way connected with the boiling point of its material and is a result of the ionization process rather than the cause of it. The facts quoted above are not, of course, intended to disprove the influence of high temperature on ionization, which is too well proven in other cases. In arcs in metallic vapors considered here, the temperature of the cathode does not seem to be the ionizing agent.

The time has not yet come to give a complete theory of the arc. In working for years with the mercury arc I had, however, to make for my own use some working hypothesis, and as this hypothesis seems to agree with all the facts that I have observed and was helpful to me in the course of my investigation, I will outline it here briefly, without, however, trying to give in detail its justification, as this would require an article for itself. In some points this hypothesis agrees with the views of previous investigators, in some others it differs.

Starting from the hypothesis developed by a number of modern scientists, according to which the conduction in metals is due mostly to the negative electrons, and from the postulate that the mechanism of conduction in different states of matter must have the same general characteristics, I assume that the mechanism of the conduction in the arc is similar to that in metals and that an *arc is, electrically considered, in the main a flow of negative electrons directed from the cathode toward the anode.* While in the metal the number of electrons is a given quantity and the conductivity accordingly constant, the number of electrons *crossing the surface of the cathode and entering into the arc must be proportional to the current. Accordingly, the conductivity of the arc is proportional to the current.* The process of starting an arc serves to initiate the process by which the electrons

are driven out from the metal into the space. The starting is probably produced by purely electrical causes. If this process, by means of which the negative electrons are projected out of the metallic mass is started, it goes on of itself so long as a sufficient amount of energy is supplied. The disintegration of the cathode is a mechanical accompaniment of this electrical process.

The light emitted by the arc is not due directly to the radiation of the electrons. These negative electrons are probably the same in all arcs, and the light emitted changes according to the molecular material through which these electrons move.

Schenectady, N. Y.
March 31, 1905.

DISCUSSION.

PRESIDENT CARHART: Doubtless you have many questions to ask. We shall be obliged to make matters brief.

DR. WEINTRAUB: I made a number of experiments on the transfer of matter in the mercury arc. The mercury arc represents simpler conditions than any other arc, because it takes place in a vacuum and the material used undergoes no chemical or physical change. I found that the amount of material that is transferred from the cathode to the anode is so small that it forms only a very small part of that required by Faraday law. I could not make sure, however, that this transfer is not due to mere volatilization and diffusion.

PROF. FRANKLIN: May I ask Dr. Weintraub what he meant by that last statement? Does he mean to say that the amount of transfer is less than that calculated by Faraday's law on the assumption that the ratio of charge to mass is that of hydrogen ions?

DR. WEINTRAUB: The amount transferred to the anode, under the assumption that the ions do not move also in the direction from anode to cathode, is only one-thousandth to one-millionth of the amount calculated.

PROF. FRANKLIN: So that even though you were to take the ions which constitute cathode rays (that is, electrons), the calculated transfer would still be greater than the observed?

DR. WEINTRAUB: It may well be that the value is of the order of magnitude required by the value for the electron mass accepted in modern theories.

PROF. FRANKLIN: There is an interesting point in connection with the transfer of material by electrons. A number of years ago I got it into my head that perhaps the Crookes discharge through mercury would represent the disintegration of mercury and a formation of new elements. I set up an apparatus in 1896 for making this experiment; afterwards I got some data on the mass of the electrons from J. J. Thomson's paper, and I calculated that with the amount of current passing through a Crookes tube that I had it would take me about a thousand years to transfer a milligramme of material; so I stopped.

PRESIDENT CARHART: We will not have time during this session, I am afraid, to settle that question. There are two or three papers which have been printed and which we have not been able to call for. Perhaps some one would like to make a remark respecting them.

A paper read at the Seventh General Meeting of the American Electrochemical Society, held at Boston, Mass., April 27, 1905. President Carhart in the chair.

ARCS.

By W. R. Whitney.

The purpose of this paper is a brief review of the phenomena occurring in an electric arc, with especial reference to the migration of material comparable with electrolytic migration.

In 1800 the voltaic pile was invented, and probably in 1802 the first electric arc was observed between carbon terminals by Sir Humphrey Davy. Using a battery of 2,000 cells, he formed an arc between charcoal points which was four inches long. It was over forty years later that any appreciable attempts were made to utilize the light thus produced. The whole scheme for practical utility had to await the development of mechanical apparatus for generating the electrical energy which had previously been generated by batteries alone. The present direct current open carbon arc is still practically nothing more than the simple combination then used, with the exception that refined forms of carbon, instead of charcoal, are used as electrodes.

It was early noted that the greater part of the light comes from the tip of the positive electrode, and for this reason the positive is usually placed above the negative, so that the light of a suspended lamp is utilized to the best advantage.

The electrodes of an open arc on burning soon assume characteristic forms; the upper positive becomes cup shaped, or a crater is formed in it; the lower becomes pointed on burning. It is the common belief that the crater of the positive is heated to the vaporizing point of carbon and therefore its temperature is of interest. This temperature has been carefully measured by Weidner and Burgess, and by many others, and it appears that the most accurate methods show a temperature of about 3,700°C. It is worthy of note that so short a time ago as 1880 the best authority, Dewar, gave 6,000°C as the arc temperature.

Mrs. Ayrton has written a book of nearly 500 pages on the direct current carbon arc alone, and yet there still seems to be

much to be learned about it. Other arcs than carbon have not received much attention. We merely wish at this time to call attention to some of the simpler peculiarities of different arcs, and, if possible, to co-ordinate some of the facts which we may obtain thereby, and we would like to show how little has been really yet learned about the actual phenomena in an arc.

We project on the screen, by means of a simple lens, the image of a direct current carbon arc. This arc consumes about 5 ampères at 60 volts,or 300 watts, but it requires what is called a steadying resistance in series with it, to counteract the negative temperature co-efficient of resistance of the arc itself, so that a single lamp at 5 ampères on 110 volt circuit actually consumes 550 watts instead of 300. A source of electromotive force just equal to that which would be found on measuring the drop across the arc would not maintain the arc itself. There must be an extra resistance in the circuit, and this is greater the greater the length of the arc, and is also greater the lower the current. The arc represents a peculiar conductor. In the first place, we may say that it acts like a conductor at whose terminals there is a voltage opposing the impressed electromotive force. It seems like a combination of storage battery and resistance, but is even still more complex, for the resistance itself is variable, and diminishes as the current rises.

Professor Ayrton and others have measured the distribution of the potential drop through the carbon arc by interposing exploring carbon pencils. They have concluded that there is a drop of about 35 volts at the positive electrode and about 9 volts at the negative. These values are not quite independent of the length of the arc nor of the current employed. While there is an apparent counter electromotive force equal to about 44 volts, the drop through the arc varies from 1 to 28 volts, depending on the length and current. In general, the higher the current for a given length the less the resistance of the arc path. It must always strike the uninitiated as peculiar that in an arc lamp a certain definite quantity of energy must be consumed distinctly apart from the arc itself. In other words, the arc cannot operate on the voltage and current which it actually consumes, but always requires the consumption elsewhere in the circuit of a considerable quantity of energy, which may amount to 10 or 20 per cent. of that consumed in the arc.

As electrochemists, we are probably most concerned with the phenomena of conduction of the arc and the chemistry of the effect of various elements on the luminosity of the arc, and we will devote the rest of this paper to that subject.

It is most tempting to treat the subject of different arcs on the basis of some tentative theory, and if on our generalizations no undue weight is laid, there may be some instructive analogies suggested. It is natural to seek mechanical conception of the current phenomena in arcs, and this ought always to assist in the study of their luminosity. Such useful information on the electric current has resulted from the work of Faraday on the passage of current between electrodes in solution that we are led to attempt the simplest analogy in the arc. In the former case we know that the current may be said to pass between the electrodes as material ions holding electric charges, and that in general both positive and negative ions move between the electrodes. Moreover, in no case is the distribution between positive and negative current equal. Either the one or the other kind of ion moves with greater velocity. In the electrolytes we have also learned to differentiate between the process of current passage and the phenomena which occur directly at the electrode surface. Are we to find a similar condition in the electric arc? It seems certainly too early to answer this question, but for the purpose of establishing a view of the phenomena of ordinary arcs let us first assume a passage of electrically charged ions in a single direction only. Owing to peculiarities which are common to arcs and to which we will later refer, it seems simpler to start with the assumption that the current is carried across the gap between the electrodes as negatively charged particles or ions; that is, by ions supplied by the cathode in every case.

This assumption is the simplest that could be made if any loss of electrode material is necessary during the passage of the arc. It has been a common conception, since the work of Hare and Silliman, that the current either entirely or principally crosses the arc as positively charged particles. This idea was due to the fact that the positive electrode in a carbon arc wastes away more rapidly than the negative, and that the wasting positive is cratered or pitted, while the negative is usually pointed. Apparently all recent investigators have felt obliged to assume a pass-

age of charged material in both directions through the arc, about as we now conceive of the passage of electric current through a solution. The establishment of this idea experimentally is much more difficult than at first imagined. In the many cases described in the literature it was not possible to exclude the simple distillation or sublimation of the material from either electrode, so that, for example, in the experiment of Von Breda, an are between a copper and an iron electrode usually resulted in iron being afterwards found on the copper and copper on the iron. At the temperature of the arc either of the metals could easily have sublimed, regardless of current phenomena. Such arcs in air always exhibit burning metal vapor about the electrodes. I do not find any reason for assuming any migration of material from a positive electrode in an arc, and for a few moments I wish to consider the assumption of a flow of negative particles only in all arcs, although I consider this merely a step which the facts may later force us to retrace. It is true, however, that the assumption of a flow of negative ions helps in co-ordinating the general phenomena of arcs.

In the carbon arc the negative electrode always wastes away, but slowly; the positive burns away in air and may even distill, as it is the hotter of the two. It is, however, the negative electrode which is always used up, no matter how low its temperature may be kept. If we accepted the assumption that the negative ions carry the current we would look at the highly heated crater of the positive as owing its temperature to the impact of the negative particles from the cathode. In this case we would expect an arc proper to have the color and properties of a carbon arc so long as the negative electrode was carbon; that is, it should make no difference what was used as positive electrode. This is in general quite true, though here we find special phenomena which at least cloud the issue. If we substitute for the anode of the carbon arc an electrode of iron, or any other metal of high melting point and low vapor tension, we find that the arc is still characteristic of carbon. If, now, we reverse the current we notice that the arc is characteristic of an iron arc, at least throughout a part of its path, and the path itself is very much more luminous than before. Similarly we may observe the characteristic arcs of magnetite and of copper by using these two elec-

trodes as cathode against the other as anode. This is still a very imperfect method, for there is no evidence that the color of the arc is due to the conducting ions, if, in fact, there be any such ions. It is evident that the effect of heat alone on the vapors and on the suspended solids which may exist in the arc should produce the characteristic colors observed, and one would therefore expect that under similar conditions the spectrum of the arc might be independent of the current phenomena. In the case of carbon electrodes which contain volatile salts, such as calcium fluoride, the light of the arc is much greater when the anode contains the salt than when the cathode contains it. The anode in this case is hotter and the light effect is probably largely due to the higher rate of evaporation. By the introduction of various salts into carbon electrodes the light of the arc has been greatly increased for the same energy input, but the rate of consumption of the electrodes is practically that of carbon, and, owing to the fact that enclosing globes cannot be used, such impregnated carbons are only useful in open arc lamps which are daily trimmed.

When the arc passes between electrodes which do not undergo appreciable combustion, as in the case of oxide of iron, in the air, the negative electrode alone wastes away, while the positive may even increase in weight. This is one of the facts which makes us prefer to assume the necessity of negative ions in the arc instead of positive ones. In the mercury arc the cathode also feeds the arc, and the anode may be any conductor without affecting the characteristics of the arc. On the other hand, any other cathode than mercury in a mercury atmosphere is slowly consumed just as in other arcs, and the same holds true with such arcs as sodium in vacuo. This has been pointed out by Dr. Weintraub.

In the case of the mercury arc the resistance is diminished as the current increases; that is, the potential drop across the arc remains almost constant during moderate changes of current. In the case of other arcs, such as carbon in air, this is also true when the current is above a certain value. At low current the voltage necessary to maintain a carbon arc of given length increases as the current decreases. These facts may be considered as coinciding with the conception of ions whose motion across the gap constitutes the current. An increase of current

would thus be conceived as not due to more rapid motion of ions than in the case of feebler current, but to a greater number of the ions themselves, the specific resistance of their motion being nearly constant. At low currents the relative effect of cooling the path of the arc might be predominant and account for the necessary high voltage when the number of conducting particles is greatly diminished. What is true of the carbon arc in this respect seems also to be true of all other arcs in air, such as metal and metallic oxide arcs.

It might be thought that by a proper selection of non-combustible cathodes the Faraday equivalent for current in the arc could be determined, but, just as in the case of the mercury arc, as is shown by Dr. Weintraub, we obtain little more than evidence that the electrochemical equivalent, if there be any, is much less than in ordinary electrolysis. For example, a pair of pure magnetite electrodes were used in an arc of 3 ampères and the changes in weight noted. The cathode lost a little; the anode practically did not change in weight. A calculation from the data showed that at most not over one-twentieth as much material was lost from the cathode as would have passed through a solution as copper ions carrying the same current. We know now, however, that this rate of wasting of the iron oxide cathode is very greatly affected by the presence of different substances, and that in general it wastes away faster the lower its melting and vaporizing points. A mixed oxide cathode containing such materials as the rare oxides may be giving an arc characteristic of the cathode material, and only wasting away at a rate of 1 gram in five hours, at 4 ampères current. This is not far from one-thirtieth of the weight of copper which could be deposited on the cathode in a copper sulphate solution in series with this arc. Moreover, the loss in weight varies enormously with slight changes in composition of the electrodes.

This rate of consumption, which occurs only at the negative electrode, is so small that it has been found feasible in practice to operate open arc lamps with magnetite or similar electrodes for at least two weeks without renewing the electrode.

In connection with this consumption of arc electrodes we performed some experiments a few years ago which are of value, if only in assisting to establish the complexity of the question.

In the production of colloidal platinum, by running an arc between platinum electrodes under water, Bredig had shown that the cathode lost in weight. We repeated this and similar experiments with various metals and sought for the relationship between the quantity of metal which was removed from the cathode and the corresponding current. With two platinum electrodes in water at room temperature and a current of 6 ampères, the cathode lost in weight practically half as rapidly as the cathode of a copper voltameter in series with the arc gained in weight, the ratio of cathode loss to copper deposit varying from 47 to 62. In these experiments the platinum anode of the arc increased in weight by approximately one-fifth of the cathode loss, but this result was also quantitatively very irregular. Thus, about four-fifths of the platinum which was vaporized from the anode remained suspended in the water. With copper and with gold subaqueous arcs, the cathode also decreased in weight, and the anode usually, but often only very slightly, increased in weight. Copper as cathode of the arc lost about five-thousandths as rapidly as the copper cathode of the voltameter in series gained in weight.

From these results on sub-aqueous arcs alone, we may conclude that it seems necessary for arcs to lose material from the cathode during operation; that the anode need not change, though it may gain in weight; that the Faraday equivalent is not concerned in the process, and that far the greater part, if not all the material leaving the cathode need not be deposited on or even reach the anode. If, then, this current is carried across the arc gap by particles of metal, it is most probably by negative particles, and during the process the excess of the material of the negative electrode is vaporized, even when this is a small wire surrounded by water.

These results would seem in strictest accord with a theory which merely postulates the passage of something from the negative to the positive electrode, which something may be relatively small compared to material vaporized, or may even be without weight, as suggested by Dr. Weintraub. Because of this separation from the cathode, weighable quantities of this electrode may be simply vaporized or perhaps mechanically removed.

We must recognize a certain similarity between such experiments and the action of the ordinary Geissler or cathode ray

tube. In these cases the cathode gradually wastes away, the anode is unaffected and the particles shot from the cathode do not proceed to the anode, but move in straight lines to the walls of the tube. Much work has been done on this class of migration, but no significant relationship has yet been found between the electric discharge and the quantitative loss of the cathode. In other words, the spattering, the vaporization of an arc, may be independent of the current.

Experiments performed by Dr. Weedon, and described in a previous number of this Journal, also show conclusively that at least in the case of some arcs the actual necessary loss of either electrode is exceedingly small. This is particularly true in the case of arcs running in *vacuo*. That the air or gas between the electrodes may play an important role in the phenomena of the arc is well known, but that any part of the current is actually carried by ions of the gas is not certainly known. Most arcs burn about as readily in nitrogen as in air. They do not burn so readily in hydrogen, but this may be due to the greater heat conductivity of this gas. They also burn in *vacuo,* so that it is not necessary that another conductor than the electrode material should be present. On the other hand, when a gas is present it may show its characteristic spectrum, as an experiment of Dr. Weintraub's has shown. In this case an arc produced between carbon points in mercury vapor was a characteristic mercury arc, although the carbon cathode wasted away.

An interesting experiment which may have some bearing on the direction of the ions of the arc has been described by Fleming. A small third carbon is introduced into a carbon arc between the two electrodes, and it was found that this carbon assumed the potential of the cathode, so that on connecting it with the anode a current flowed from the new carbon to the anode, but no current would flow through the circuit connecting the third carbon with the cathode. Fleming concluded from this experiment that negative carbon particles carrying the current pass from the cathode to the third carbon and to the anode, the impact of these particles on the anode causing its heating and the vaporization. It has long been known that hot carbon, such as a filament in an incandescent lamp, discharges electrically to a metal conductor in the lamp. If, then, hot carbon discharges negative

ions more easily than positive, the first step in forming an arc would seem to be a negative discharge, and this has been pointed out by J. J. Thomson. He, however, goes farther, and assumes that the negative discharge, which heats the anode by impact, ionizes the gases in its vicinity, giving positive ions, which also take part in the passage of the current across the gap.

There are many reasons in connection with the discharge in gases why this is a useful theory, but there are also difficulties which ought to be recognized. So far as we know, it has not been found possible to interfere with the arc by keeping the anode perfectly cold. Dr. Weintraub has also shown that a cathode may be kept cold without any effect on the arc itself.

We cannot prove, then, a definite necessary connection between moving material and electric current in the arc. They act as though they were simply two accidental accompaniments each of the other. If we were to give up the idea of matter moving with the negative current in the arc one might say that there would then be no reason that positive ions should not also carry the current. The reasons for not expecting this at once are that in the study of ions thus far, the negative ion has been shown to be more mobile than the positive, and the losses, when they do occur at electrodes, in the arc, most persistently occur at the cathode. Fleming's experiment with the third carbon and the fact that an arc may simultaneously flow from one cathode to many anodes, but not from one anode to more than one cathode, influences the choice in this case. We are inclined to believe that no necessary connection exists between the loss of electrodes and the current passing between them.

Research Laboratory,
General Elec. Co.

A paper read at the Seventh General Meeting of the American Electrochemical Society, held at Boston, Mass., April 27, 1905. President Carhart in the chair.

THE ELECTROLYTIC PRECIPITATION OF NICKEL ON NICKEL

By Ralph C. Snowdon.

It has been noticed in many books on technical electroplating that nickeled work which is to be replated must be entirely freed from the previous deposit of nickel or the subsequent plating will be in vain. McMillan says in regard to this: "It is even more important in nickeling than in silvering or gilding that an existing film of nickel shall be entirely removed, or the new deposit will most certainly lack adhesive properties."[1] He[2] also mentions that suspending wires should be used but once because the subsequent deposits of nickel will peel off and give trouble in the bath. This peeling also causes thick deposits of nickel to be rather undesirable.[3]

Burgess and Hambuechen[4] have noticed this peeling and non-adherence in the case of other deposits, and they say: "A peculiarity, the reason for which does not seem to have been explained, is that a metal, by contact with the plating electrolyte itself, may change the character of its surface to such an extent that a coating subsequently deposited will not adhere firmly to it. We have observed during an investigation on the electrodeposition of iron, that if the iron cathodes are allowed to remain for a few hours in the solution without the flow of current, a subsequent deposition of iron will take place, but the layer thus deposited may be readily separated from the previous layer. . . . The same phenomenon has previously been pointed out in the electrolytic separation of nickel."

The real reason why the deposit curls up any more than the same metal would if it were not electrolytically prepared seems to be due to the metal being deposited in a state of strain which is

[1] McMillan, A Treatise on Electrometallurgy, 2d ed., p. 243.
[2] Ibid, p. 245.
[3] Ibid, p. 246.
[4] Jour. Phys. Chem. 7, 409 (1903).

undoubtedly caused by absorbed hydrogen[1] or uneven deposition of the metal.[2] There is no evidence that an hydride of nickel is formed. This would hardly account for the fact that the original metal and the deposit do not adhere. Prof. Bancroft suggested that the first metal had become covered with a film of some oxide which could not be removed by ordinary methods of cleaning, or, in other words, the surface was made "passive."

The reaction undoubtedly takes place with great readiness in the case of nickel, iron and aluminum, according to Burgess and Hambuechen.[3] Therefore, if this surface be treated with some strong reducing agent, we should have a metal free from oxide which would take an adherent deposit if it were transferred immediately to a plating bath through which current is flowing. The most convenient way in which to do this is by making the passive metal cathode in an acid solution and passing a fairly large current for a short time. This will cause a heavy evolution of nascent hydrogen, part of which will be taken up by the metal and the oxide will be reduced. Quick washing and transferring to the plating bath should give us a metallic surface upon which an adherent deposit could be plated.

For the preliminary treatment of the nickel cathodes, we prepared a 3 normal solution of hydrochloric acid and used a current density of 8 ampères per square decimeter. The electrodes were both of nickel and were placed about 4.25 cm. apart. The run lasted four minutes. Hydrogen was evolved copiously at the cathode. As soon as sufficient treatment had been given the cathode it was washed in clean water and plunged into the regular plating solution, which was made up:

Nickel ammonium sulphate, 6 aq.....80 g.
Water ..... 1 liter.

The other conditions:

Area cathode .....¼ dm^2.
Current density ....2.0 amp/dm^2.
Voltage .....3.8 volts.
Temperature .....18°.
Time .....½ hour.

[1] W. McA. Johnson. Trans. Am. Electrochem. Soc. *3*, 255 (1903).
[2] D. H. Browne, Electrochemical Industry, *1*, 348 (1903).
[3] Jour. Phys. Chem. *7*, 409 (1903).

In case a rolled nickel anode is used, the solution must be kept neutral or only very slightly acid by means of ammonium hydroxide. Too great acidity causes the precipitation of a spongy deposit. In our case the deposit came out perfectly smooth and so adherent that it could be burnished and scratch-brushed with impunity.

In order to demonstrate the difference between a prepared or "active" cathode and one ordinarily cleaned, we performed another experiment under precisely the same conditions as before, but simply scratch-brushed and cleaned the nickel plate before making it cathode. On removing from the plating solution about half the precipitated nickel had curled up, a slight rubbing causing it to fall off.

Therefore the conclusions to be drawn from this paper are:

1. Nickel can be precipitated upon the "active" nickel cathode and caused to adhere without difficulty.

2. Nickel cannot be successfully plated on other nickel because of the pressure of a thin film of oxide which cannot be removed except by rigorous reduction.

3. The "active" state is very instable.

This work was suggested by Prof. Bancroft and carried out under his direction.

Cornell University.

A paper read at the Seventh General Meeting of the American Electrochemical Society, held at Boston, Mass., April 27, 1905. President Carhart in the chair.

AN OPTICAL METHOD FOR OBSERVING THE DIFFUSION IN ELECTROLYTES.

By Carl Hambuechen.

A great deal of investigation has been directed within recent years to the study of the relationship existing between the composition of the electrolyte and the character of the deposition which may be obtained from it. It is known that the quality of deposit depends upon the chemical compositions of the solution, current density, temperature, nature of the anode material, viscosity, and the diffusion of the solution surrounding the anode and cathode.

The study of diffusion in an electrolytic cell has not received the attention which it should, and certain erroneous conceptions are held in regard to it. One of these is that we have a gradual change of density from the anode to the cathode produced by the migration of the ions. Whatever differences of density there may be, however, at the immediate surfaces of the electrodes, there is almost no variation in density on a horizontal line extending across the cell. In all active electrolytic cells there is a continual systematic movement of the electrolyte aside from that caused by gases which may be liberated, and it is for the purpose of observing this movement of the electrolyte that the method of investigation described in this paper was adopted.

If a narrow glass vessel, containing a light liquid, superposed upon a heavier one, be placed in the path of light from a projection lantern, the image on the screen will show a distinct line between the two solutions, even though the eye cannot detect it within the cell. This line is produced on the screen through differences in the refraction of the light as it passes through the solution of non-uniform density.

A glass vessel of dimensions shown in Fig. 1 was filled with a solution of iron sulphate, and two iron electrodes, A and C, were suspended therein. The cell was made of such size that it

could be placed as a slide in a stereopticon lantern, and, upon focusing, a good image of the cell was thrown upon the screen. Before the passage of current, no disturbance or non-uniformity of electrolyte was noted, but upon passing three-tenths of an ampère for a few minutes, definite horizontal lines appeared,

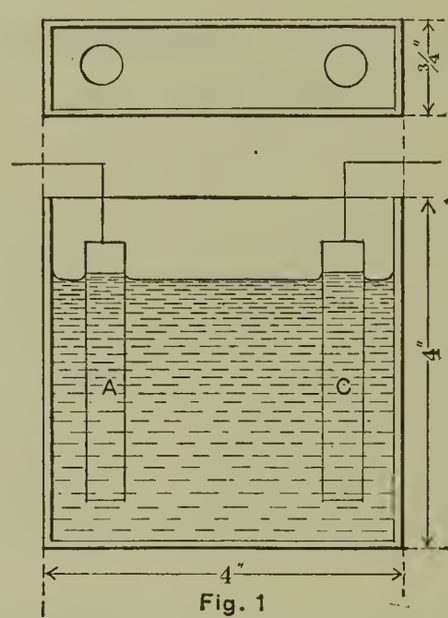

Fig. 1

extending from the anode to the cathode, indicating that the solution had become stratified by layers of different concentration, the lighter layers being at the top of the cell and the heavier ones at the bottom. In this experiment the lines were first seen to form at the bottom of the cell and gradually rise to the top. A

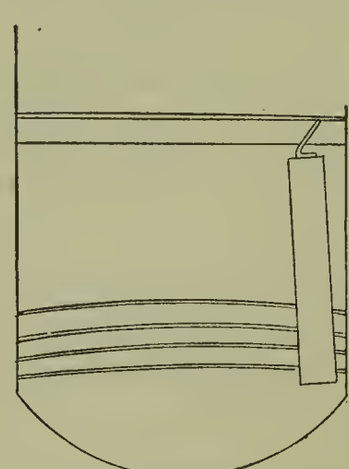
Fig. 2

stream of heavy anode solution could be observed flowing to the bottom of the cell, and the lighter cathode solution flowing in a steady stream to the top.

Fig. 2 is a photograph showing the stratification of such solution, in which the horizontal lines caused by the difference in the

refraction of the light, and also the heavy anode solution streaming to the bottom, can be noted.

By studying the stratification of an electrolyte produced in this manner a number of the difficulties encountered in the electrodeposition of metals can be explained. The rapid rising of the cathode solution explains the corrugated appearance which metallic deposits sometimes assume, and the non-uniformity in the density of the electrolyte explains the differences in the appearance of the deposit at different parts of the cathode.

By tracing out in a cell of this sort the paths taken by the solution, methods can be easily devised for altering such paths so as to meet practical requirements by means of suitable baffle plates or by an arrangement of electrodes.

Laboratory of Applied Electrochemistry,
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A paper read at the Seventh General Meeting of the American Electrochemical Society, held at Boston, Mass., April 25, 1905. President Carhart in the chair.

THE ALUMINUM ELECTROLYTIC CONDENSER.

By Clarence Irving Zimmerman.

"The Aluminum Electrolytic Condenser" was the subject of a paper by the writer at a former meeting of this Society.[1] The peculiar condenser behavior of a cell consisting of two similar asymmetrical conductors was analyzed and discussed. It was shown that the aluminum cell approximated these conditions.

In connection with these points it was mentioned that the film coating the aluminum electrodes has a thickness of from less than .000,005 cm. to, in exceptional cases, more than .000,050 cm. This result was arrived at by observing the "interference" colors presented. It was shown that under some conditions the film may have a very high disruptive strength. The various sources of energy losses were discussed, and it was stated that 110-volt condensers having efficiencies[2] of over 95% had been made. Comparisons with tinfoil condensers were made.

This paper is a continuation of the previous one. There will be presented some additional information and data relating to the above points, together with a discussion of Unsymmetrical Condensers and Polyphase Condensers.

HYDRAULIC ANALOGY OF THE ALUMINUM ELECTROLYTIC CONDENSER.[3]

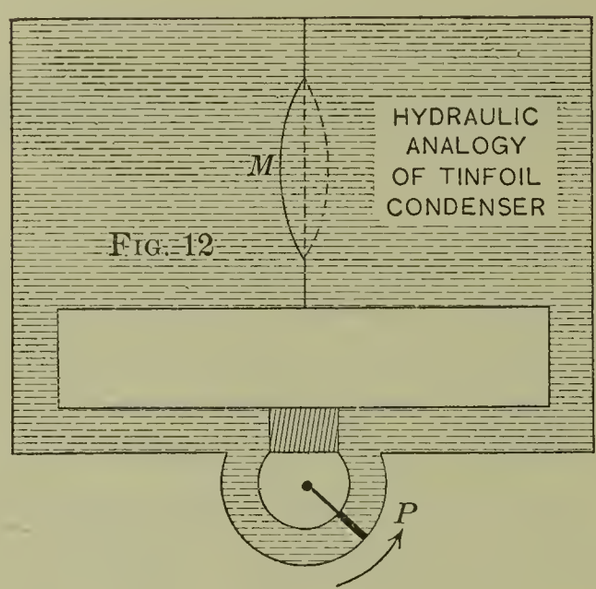
A clearer conception of the behavior of the aluminum condenser may perhaps be obtained by comparing the electrical circuits and pressures to hydraulic circuits and pressures. In Fig. 12 is shown the usual hydraulic representation of a tinfoil condenser. M is an elastic membrane and P is a pump, which by some external force of limited value causes the liquid to move

[1] "The Aluminum Electrolytic Condenser," Trans. A. E. S., Apr. 9, 1904. Vol. 5, p. 147.

[2] By "efficiency" is meant the ratio of volts x ampéres divided by volts x ampéres plus losses.—Report of A. I. E. E. Committee on Standardization, 1898—Appendix 1.

[3] Electrical Review (N. Y.), Vol. 44, No. 18, April 30, 1904.

back and forth in the hydraulic circuit. The tension in the membrane corresponds to the potential of the electrostatic coulomb charge in the film. The space traversed by the membrane



from the position of minimum surface represents the coulomb charge.

In Figure 13 two tinfoil condensers are represented in series

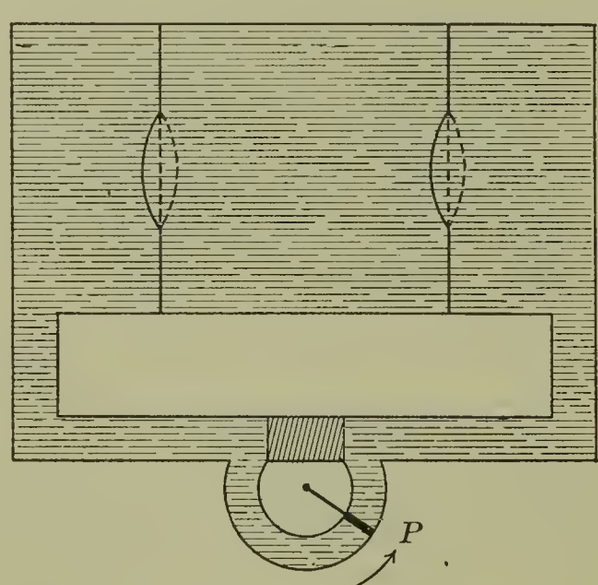


FIG. 13.

Hydraulic analogy of two aluminum condensers in series.

connection. It is a comparison of Figures 13 and 14 that the writer wishes to bring out.

In Figure 14 the aluminum condenser films or dielectrics are represented by a combination of membranes and valves. The

latter allow the liquid to flow out from the middle compartment (the electrolyte), but not into it. An examination of the tensions that must exist in the membranes will make it clear that both valves remain closed after one of the membranes has been stretched to its maximum value, no matter what lower pressure exists subsequently in the outer compartments. The instant of maximum tension in the membranes corresponds in the aluminum condenser to the instant of maximum impressed pressure. The membranes are stretched alternately, but always toward the middle compartment. The middle compartment (the electrolyte) thus remains under a lower pressure than the outer compartments (the electrodes and the electrical circuit as a whole).

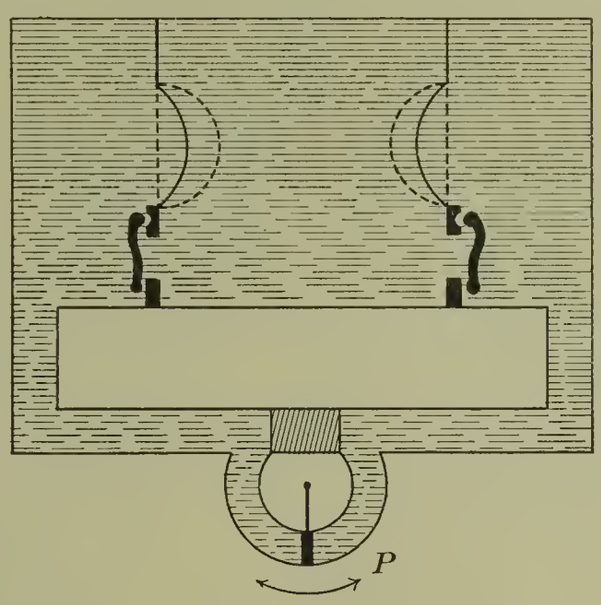


FIG. 14.

Hydraulic analogy of aluminum condenser (symmetrical cell).

RESISTANCE, DIELECTRIC STRENGTH AND INDUCTIVITY OF FILM.

The values the author gives below for the Resistance, Dielectric Strength and Inductivity are merely approximations, due to the method employed in measuring the thickness. The statements made in regard to these points in the previous paper were based upon similar calculations. Mott calculates the specific resistance of the film (as an anode film) to be of the same order as other solid dielectrics.[4] He gives an example of a certain film whose specific resistance was 10^{11} ohms per cubic centimeter. While this is somewhat lower than that of good dry insulators,

[4] Electrochem. Ind. Vol. 2, No. 9, Sept., 1904.

the author agrees with the same general conclusions if it be assumed that the leakage current is due more to the disruption of the film than to the uniform conduction of the observed current flow. The figures below give an example of results which the author has obtained with a certain film .000075 cm. thick:

Aluminum anode, 8 cm. x 12½ cm.

Area of anode, 200 sq. cm.

Electrolyte, nearly neutral solution of tartrates

$$(NH_4)_2C_4H_4O_6 + KNaC_4H_4O_6 .$$

Thickness of film, .000075 cm.

Pressure on film, 100 volts.

Current flowing, .002 amperes.

Hence, specific resistance (res. per cu. cm.) $= 1.33 \times 10^{11}$ ohms per cu. cm.

DIELECTRIC STRENGTH.

In the previous paper it was stated that the dielectric strength was apparently greater than that of mica. The dielectric strength, as calculated by the author, of numerous films upon which various pressures up to 500 volts were impressed, give results a little higher than that of 1,000,000 volts per cm. obtained by Mott.[5]

The results below indicate the values attained:

Volts withstood.	Thickness in cm.	Dielectric strength in volts per cm.
360+	.000060	6,000,000+
100+	.000020	5,000,000+
150+	.000030	5,000,000+

The dielectric strength of mica has been recently calculated to be between 1,000,000 and 2,000,000 volts per cm. for a thickness of .01 cm.[6] Steinmetz gives the gradient of 4,000,000 volts per cm. for mica at zero thickness.[7]

INDUCTIVITY OF FILM.

That the inductivity of the film is apparently high for a solid is indicated by the measurements and calculations below. The

[5] Electrochem. Ind. Vol. 2, No. 9, Sept., 1904.
[6] Electrician (Lond.), Dec. 19, 1904.
[7] Trans. A. I. E. E., Feb., 1893.

author has not attained as high a figure as 80, as might possibly have been inferred from the previous paper.[8]

The formula for the capacity of a cell in microfarads is

$$C = \frac{K}{900000} \times \frac{S}{4\pi d}$$

where C = capacity of cell in microfarads

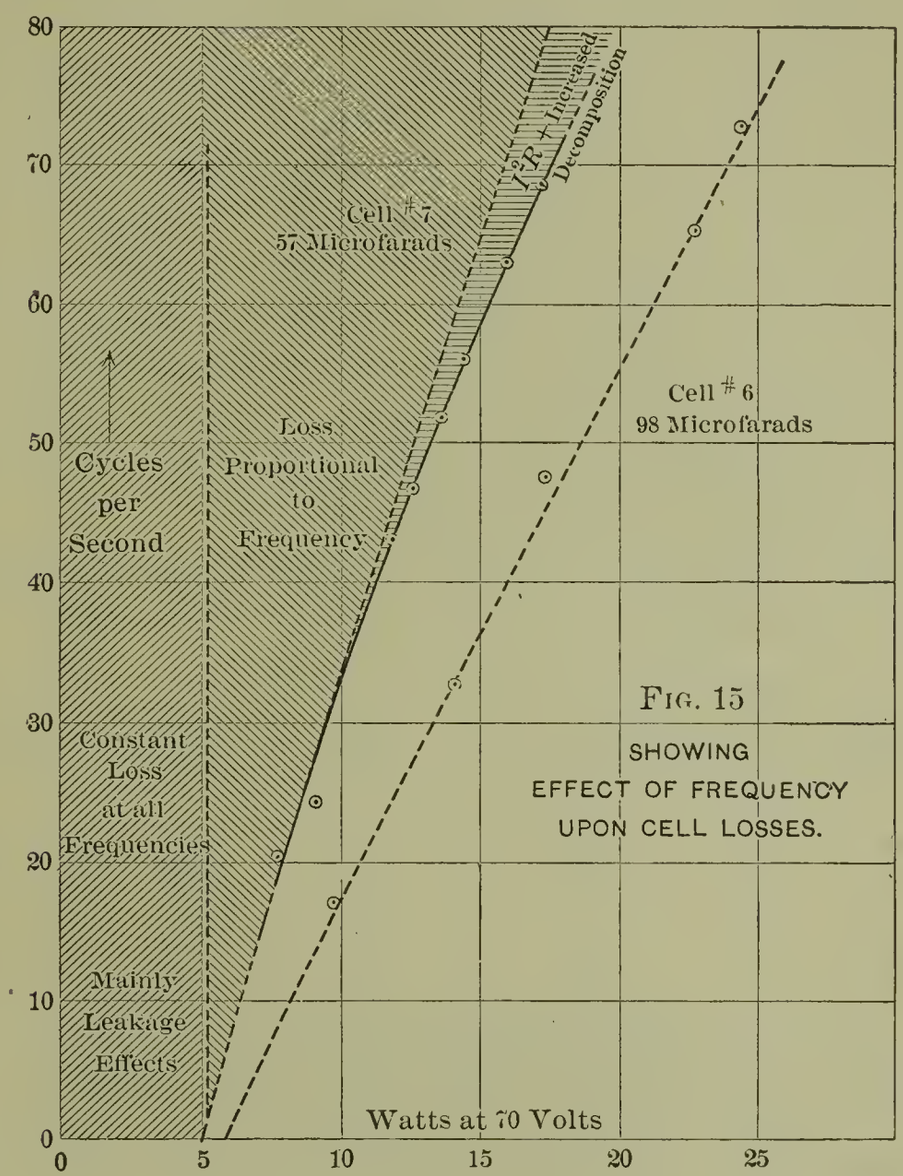


FIG. 15
SHOWING EFFECT OF FREQUENCY UPON CELL LOSSES.

K = inductivity (Specific Inductive Capacity or Dielectric Constant)

S = Area of dielectric in sq. cm.

d = thickness of dielectric in cm.

By substituting the values of C, S and d obtained from an aluminum condenser, we may obtain K, the inductivity,

[8] Trans. A. E. S. Vol. 5, 1904—p. 149.

C = 220 microfarads
S = 5,110 sq. cm.
d = .000030 centimeters.
From which the Inductivity
K = 14.6.

CELL LOSSES.

It was stated in the previous paper that the cell losses consist of (1) film losses, (2) I^2R losses, and (3) electrolytic decomposition losses; and that the film losses (1) consist of (a) leakage through film and (b) losses proportional to the frequency. The latter are in general larger than the other losses in the cell and are of a nature not clearly understood. A graphical representation of these losses is given in Figure 15, where there is plotted a curve between watts and frequency. The observations were made upon two cells in which the electrolyte consisted of an aqueous solution of commercial borax. All the losses were increased considerably by this impure electrolyte. The separate losses are graphically shown by shaded areas.[9]

That these losses can be reduced is evident from the figures on other cells made by the author, shown in the table below:

Capacity of Cell in Microfarads	Pressure on Cell (60v.)	Watts Lost	Current Flow	Efficiency
40	110	8	1.65	96.2
40	80	3	1.21	97.0
58	110	14	2.41	94.9
58	80	6	1.74	95.9

The power measurements were made with sinusoidal waves and with carefully calibrated non-inductive watt dynometer of the Siemens type. The current was measured with a Kelvin balance.

EFFECT OF FREQUENCY ON CHARGING CURRENT.

That the condenser charging current varies in proportion to the frequency is shown by Figure 16, where the impressed pres-

[9] While the values of the frequency and the power were plotted from careful measurements on a certain low efficiency cell, the exact limits of the shading as shown in the figure are to be considered only as an aid to a clear understanding, and not as an accurate separation of them.

sure is kept constant and the frequency varied. At low frequencies, however, the watt consumption shows a slight deviation from a straight line law, due to the predominating effect of the leakage current. At the higher frequencies, the capacity component practically suppresses the power component.

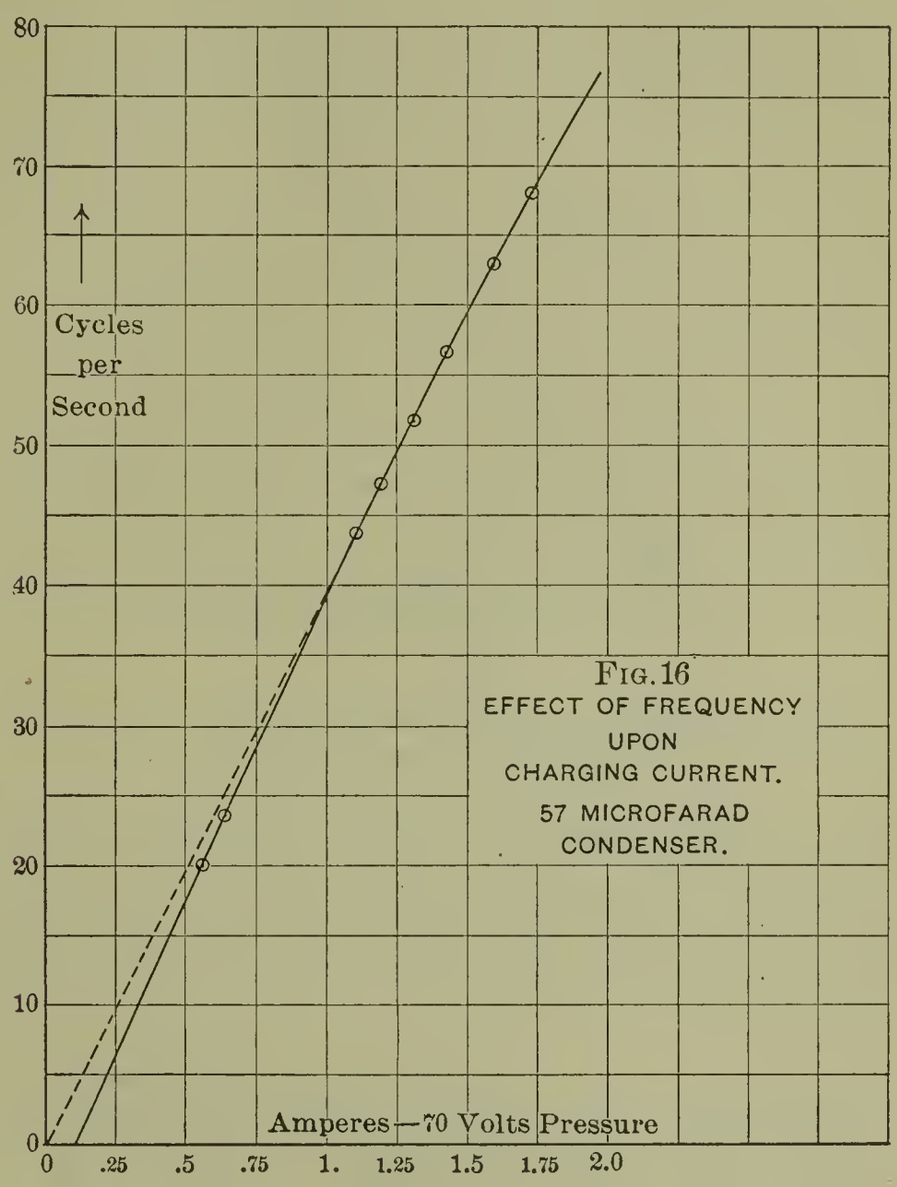


FIG. 16
EFFECT OF FREQUENCY UPON CHARGING CURRENT.
57 MICROFARAD CONDENSER.

ALTERNATING AND UNIDIRECTIONAL PRESSURES IN THE SYMMETRICAL CELL.

In the previous paper it was shown that the theoretical ratio of the alternating pressure (E) impressed upon the cell terminals to the unidirectional pressure between the electrolyte and a point neutral to the alternating pressure is equal to the impressed pressure (E) divided by the $\sqrt{2}$. The actual values obtained are smaller than these, due chiefly to the imperfect asymmetry and

partially to the cell resistance, to film leakage, and to electrolytic polarization pressures.

Figure 17 shows the relations existing in a cell each of whose plates had a capacity of 114 microfarads. The electrolyte con-

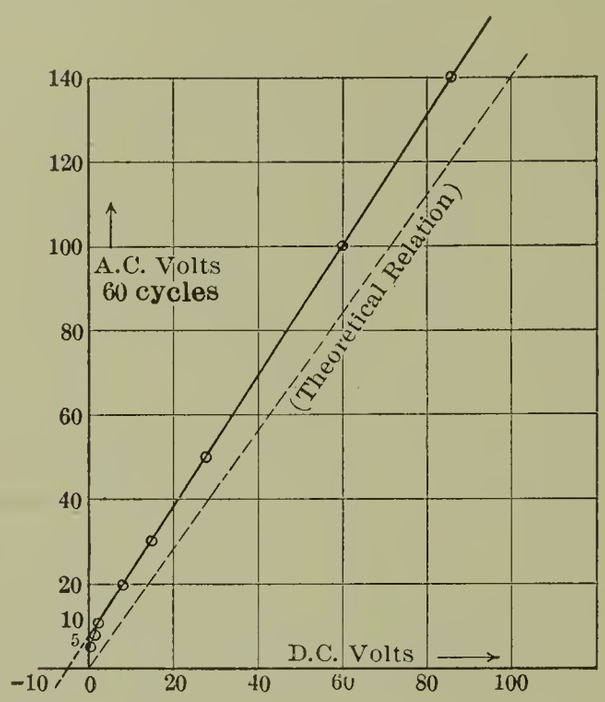


FIG. 17.

Relation between A. C. impressed volts, and D. C. volts across each electrode in a symmetrical cell.

sisted of a saturated solution of borax with a small amount of glycerine added. The method of obtaining these pressure relations is shown in Figure 18. The A. C. 60 cycle pressure was varied from 140 volts to a fraction of a volt, measurements under

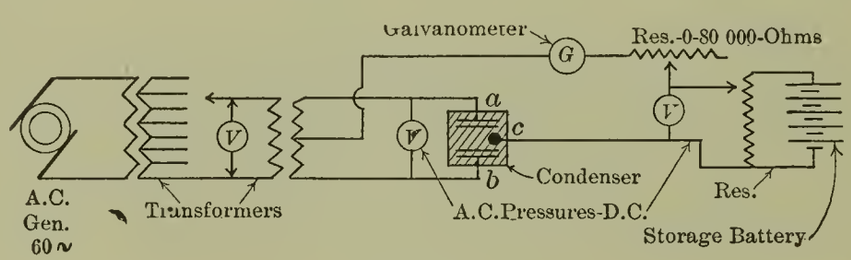


FIG. 18.

Zero method of obtaining relation between A. C. and D. C. pressures.

15 volts being made on the high voltage side of the stepdown transformer. The curve is practically a straight line above 10 volts alternating pressure. Below this point, the unidirectional pressures keep close to the zero value, owing to the slight

asymmetrical effect of the film at such low values and to the polarization pressures between the aluminum and the carbon. If the straight part of this curve be projected until it crosses the horizontal line representing the zero of alternating pressure, the unidirectional value is 4¼ volts. Part of this pressure is produced by the chain Aluminum = Electrolyte = Carbon. The dotted line in the diagram represents the theoretical relation based upon the assumption that there is perfect asymmetry, that there are no electrolytic polarization pressures, and that the losses in the cell are zero.

These pressure relations do not materially vary with any small change in frequency, and since such a cell can be easily set up, this scheme may be used for the purpose of calibrating alternating pressure instruments where extreme accuracy is not desired. It is not necessary to use the zero method, as shown in Figure 16, for the purpose of calibration, it being merely necessary to connect the alternating current instruments across the cell terminals and the direct current instruments between the carbon (electrolyte) and one of the aluminum electrodes.

UNSYMMETRICAL CONDENSER.[10]

By the term unsymmetrical condenser is meant a cell having two electrodes with different electrostatic capacities. For example, we may have two plates of the same size but having different film thicknesses, or we may have electrodes of different sizes but having the same film thickness, or we may have a combination of the two.

The limiting case of an unsymmetrical condenser consists of one large electrode and an aluminum point for the small electrode. All other unsymmetrical cells may be considered to be some stage between the symmetrical and the limiting case of unsymmetrical cells.

In studying the unsymmetrical cell we have the same general rules to follow as in the symmetrical cell, namely, that the condenser behaves on an alternating current circuit like two tinfoil condensers having capacities corresponding to those of each of

[10] The term *"unsymmetrical condenser"* should not be confused with the term *"asymmetrical cell."* The latter designates an electrolytic cell composed of an electrolyte in which there is one electrode coated with a film, and one electrode which is incapable of producing an insulating film.

the aluminum electrodes, and that there is automatically stored up in the cell a constant coulomb charge. This charge distributes itself in the cell according to the direction and value of the externally impressed pressure.

In an aluminum cell it can be shown that *the coulomb charge in the cell is independent of the electrostatic capacity of the smaller electrode. It is equal to the maximum charge held by the larger electrode.* In Figure 19 is shown an unsymmetrical cell consisting of two aluminum electrodes, *a* and *b* immersed in an electrolyte, the potential of which can be measured by means of a carbon rod *c* immersed in it; *a* represents the small electrode and *b* the large electrode. Suppose the pressure in the circuit is such that the large electrode *b* is becoming positive to the

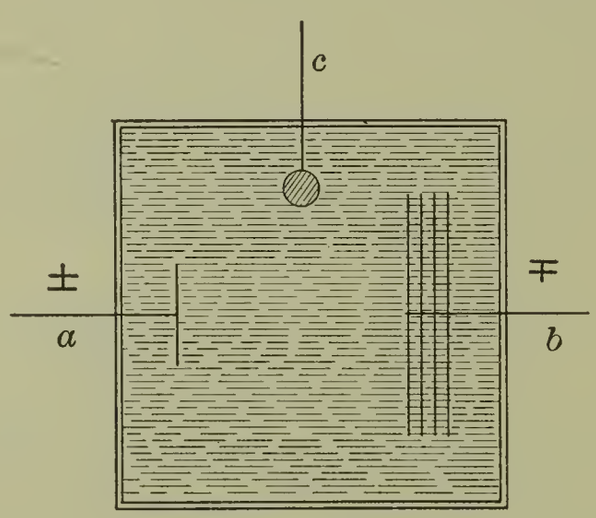


FIG 19.
Unsymmetrical cell.

small electrode *a*. Being an anode, the film of the large electrode acts as a non-conductor. A momentary flow of current occurs while its film receives an electrostatic charge. This charge is positive on the side of the film in contact with the metal and negative on the side in contact with the electrolyte. The temporary current flow finds a ready path out of the cell since the small electrode *a* allows passage in that direction. When the impressed pressure reaches its maximum value the large film becomes charged to its full extent. (This is equal to C_1E_M; where C_1 is the electrostatic capacity of the large plate and Em is the maximum value of the alternating pressure impressed upon the cell.) When the pressure decreases the charge has to remain on the large plate because the electrostatic capacity of the small electrode is negligible and

upon the reversal of the current the small electrode quickly becomes charged to its full pressure, thereby stopping the current. *When the pressure reaches its maximum value in the direction opposite to that we assumed at the start, the pressure on the large film and*

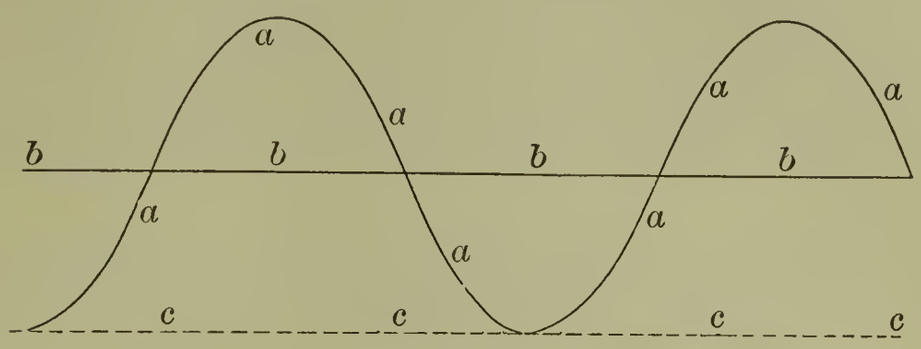


FIG. 20.

Pressure in unsymmetrical cell.

the impressed pressure act in series. Thus the pressure between the small electrode and the electrolyte reaches a theoretical maximum value of twice the maximum value of the pressure of the alternating wave upon the cell. In actual cells I have calculated that instantaneous pressures of 250 volts were reached with a

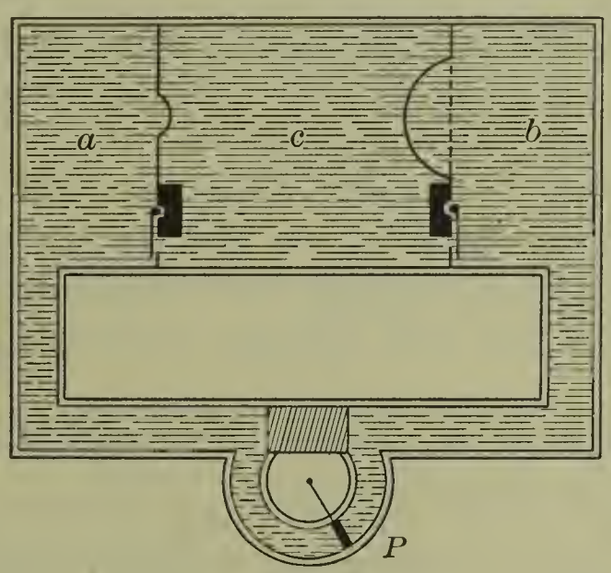


FIG. 21.

Hydraulic analogy of aluminum condenser (unsymmetrical cell).

maximum of 141 volts impressed upon the cell terminals. These calculations were based on measurements given in the table a few lines below.

This interesting point is shown graphically in Figure 20,

where *a-a* represents the potential of the large electrode, taken for reference; *b-b* is the potential of the small electrode with respect to the large one; that is, it represents the impressed pressure; *c-c* represents the potential of the electrolyte which, as we observed before, must remain negative to and at a constant potential difference from the large electrode. The pressure between the small electrode *b-b* and the electrolyte *c-c* is represented by the ordinates between the corresponding curves in Figure 20.

A cell having one electrode of negligible electrostatic capacity does not react upon an alternating pressure circuit as does an ordinary condenser. It can receive a charge, but cannot return it.

In Figure 21 is an hydraulic analogy of this limiting case of the unsymmetrical cell. With the previous hydraulic analogies in mind, this diagram is self-explanatory.

All other unsymmetrical cells consisting of one large and one small electrode of different electrostatic capacities may be represented by a similar figure. Figure 27 shows the complete range of the conditions obtainable with unsymmetrical cells.

Measurements which have been made on various cells approaching the limiting case are given in the accompanying table. They do not reach the limiting theoretical values, because (1) the small electrode in some cases had a capacity of several microfarads; (2) the measuring instruments absorb some of the charge; (3) there are cell losses; and (4) the film is not a perfect asymmetrical dielectric. These readings were obtained with various cells at different times and with different electrolytes.

PRESSURES OBSERVED IN VARIOUS UNSYMMETRICAL CONDENSERS.

(A) Capacity of Large Condenser Plate.	(B) Impressed A. C. Pressure.	(C) Pressure on Large Plate measured by A. C. Voltmeter.	(D) Pressure on Large Plate measured by D. C. Voltmeter.	(E) Pressure on Small Plate measured by A. C. Voltmeter.	(F) Pressure on Small Plate measured by D. C. Voltmeter.
(1) 8 mf.	88	85	97	121.5	96.5
(2) 8 mf.	71	68	78.5	92.5	78
(3) 12 mf.	103	110	111	144	110
(4) 12 mf.	102	104	102	143	105
(5) 12 mf.	51	60	56.5		
	50.5			79 5	57

It will be observed that the pressures in the 12 microfarad cells recorded in columns C and D and in D and F are nearly the same, showing, first, that the pressure on the large electrode is a nearly uniform unidirectional pressure, and second, that the "average" pressures on the two plates are the same.

The equations of the cell, based on the assumption that the chain "Aluminum electrode = Film = Electrolyte" is an asymmetrical dielectric are developed in a later part of this paper.

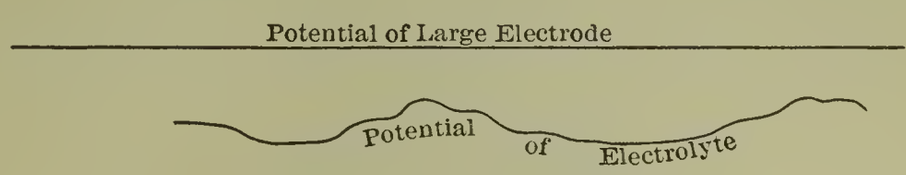


FIG. 22.

Oscillograph curve of pressure on large electrode.

Oscillograph curves of the pressures on the large and small electrodes in an unsymmetrical cell are shown in Figures 22 and 23. The impressed pressure was irregular in shape, which accounts for the irregular wave forms.

Various combinations of unsymmetrical cells may be made which will produce constant or pulsating unidirectional pressures

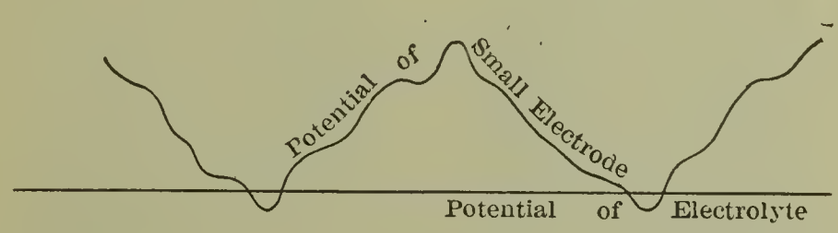


FIG. 23.

Oscillograph curve of pressure on small electrode.

up to a limit of 4.2 times the "effective" value of the alternating wave impressed upon the cell.

This is shown in Fig. 24, where by one combination of two unsymmetrical cells (placed in three vessels), unidirectional pressures having an "average" value over twice the "effective" impressed alternating pressure may be *observed* between the tops *a* and *b*. The theoretical limit is here 2.83 times the alternating pressure.

MATHEMATICAL ANALYSIS OF CELL.

The fundamental equations of the aluminum condenser differ from the corresponding equations of two tinfoil condensers in the two following points:

(1) The pressures on the two aluminum films are in opposition to one another, while the pressures on the tinfoil condensers dielectrics act in unison. (See equation 1, page 328).

(2) The sum of the coulomb charges in the aluminum cell is

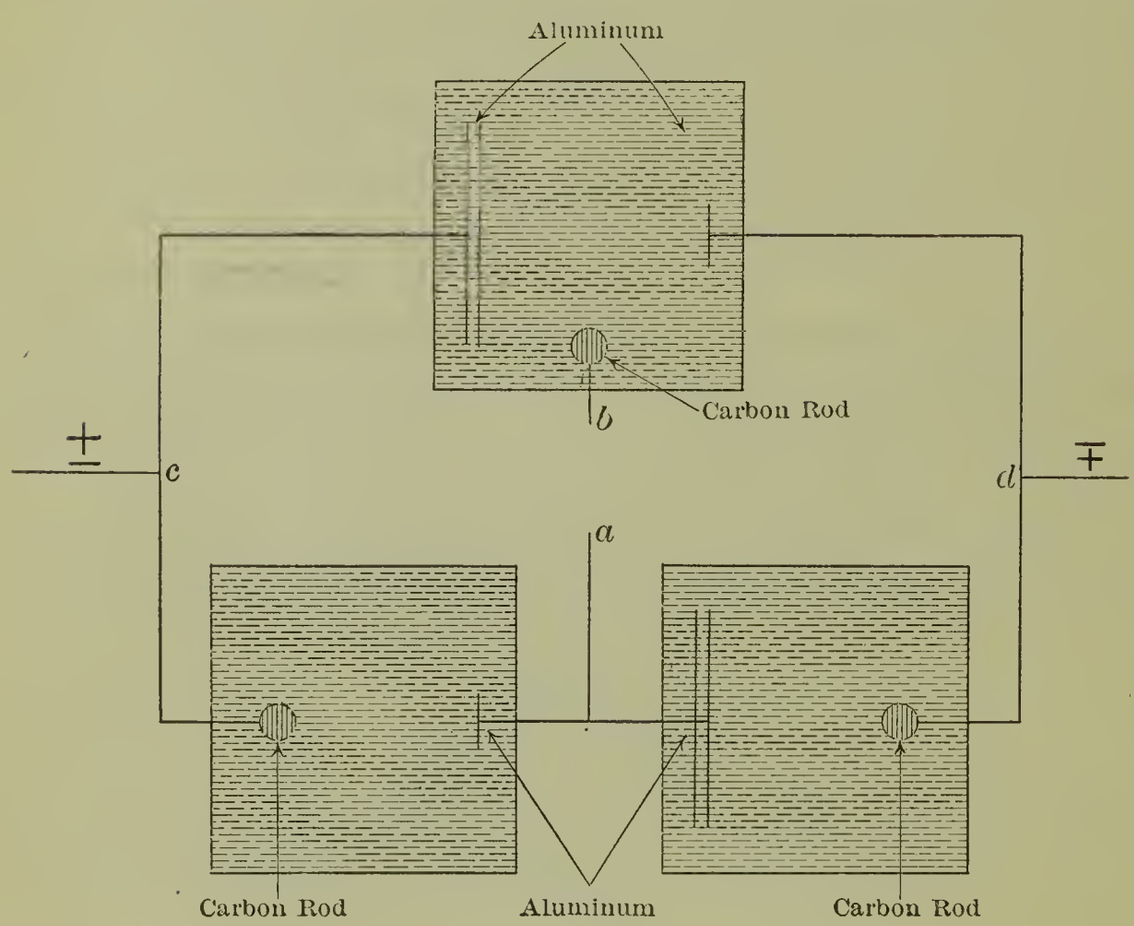


FIG. 24.

A combination of cells producing unidirectional pressures more than twice.

constant and is equal to the maximum charge capable of being held on one electrode in the cell. In the tinfoil condensers the coulomb charge varies with the pressure on the terminals. (See equation 2, page 328).

The equations, as worked out for each electrode in a later part of this paper, show the instantaneous values of the film pressures, coulomb charges and energy charges, and the "average" and "effective" pressures on each film (corresponding to D. C. and

A. C. voltmeter deflections). It is shown finally that the "equivalent" capacity of an aluminum cell is $\frac{c_1 c_2}{c_1 + c_2}$, where c_1 and c_2 are to electrostatic capacities of the two dielectrics. This ratio is also the equivalent capacity of two tinfoil condensers operating in series, the condensers having capacities c_1 and c_2. The result emphasizes the point that on an alternating pressure circuit a condenser composed of two asymmetrical electrodes acts like two tinfoil condensers, having equivalent electrostatic capacities connected in series. The "internal" conditions, however, are quite different.

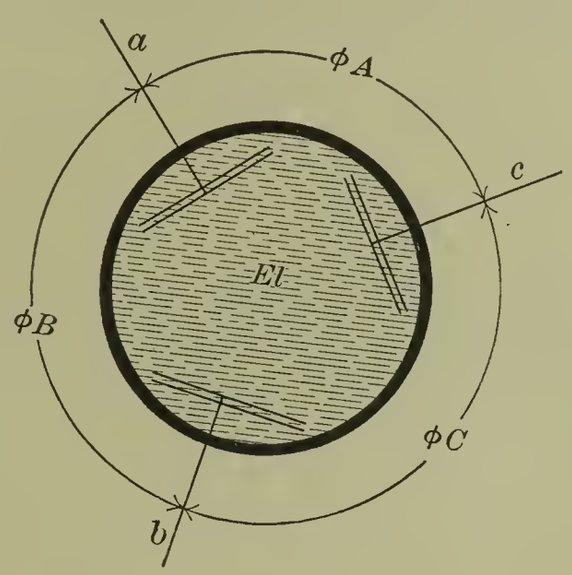


FIG. 25.

Three-phase condenser.

POLYPHASE CELLS.

In the polyphase condensers the same general rules that apply to single phase condensers hold good, but some additional points relative to them will be mentioned. On a two-phase independent four-wire circuit an aluminum condenser consisting of four plates immersed in the same electrolyte may be used. Neither circuit will interfere with the other.

On a three-wire two-phase circuit a three-plate single-cell condenser causes a charging current to flow not only in the two phases, but in the phase formed by the two independent wires of the three-wire system. The pressure between these two wires is considerably greater than the pressure of the normal phase. This extra wattless current, such a cell might be objectionable on a two-phase three-wire circuit.

In a three-phase condenser (see Figure 25), consisting of three similar plates in a single cell, we have an interesting problem for solution. The properties of this cell are briefly summarized below.

The sum of the coulomb charges on the three plates is constant, and is equal to the maximum charge capable of being held by the cell with a given impressed pressure.

This maximum charge does not collect at a time when the pressure across two of the plates is a maximum, as it does in the single phase condenser. It collects when two of the three plates are at an equal positive potential with respect to the third plate. This point is shown in Figure 26 at the point o-o. The constant

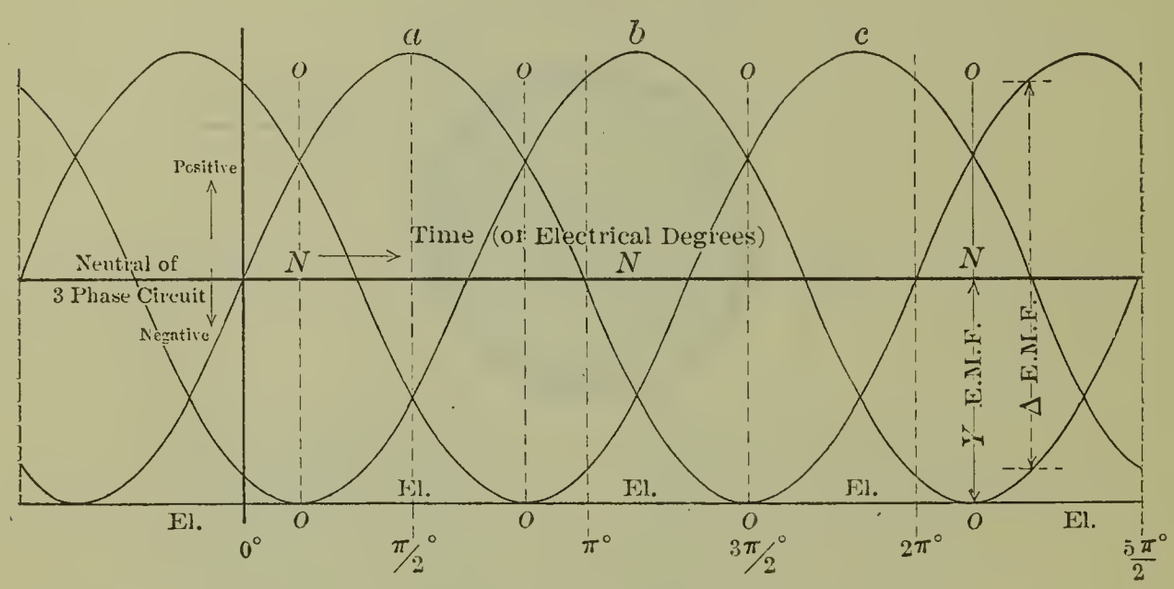


FIG. 26.

Three-phase condenser pressures.

coulomb charge is equal to $(2C)\sqrt{3}/\sqrt{2}$ E, where C is equal to the electrostatic capacity of one of the three similar plates and E, is the delta A. C. pressure impressed upon the cell.

This coulomb charge theoretically sets up a constant unidirectional pressure between the electrolyte and the "neutral" point of the three-phase circuit. The pressure is equal to the maximum value of the "star" voltage of the circuit or its equivalent.

If one of the three electrodes be disconnected from the circuit, the constant unidirectional pressure drops to the normal single phase value. This is equal to $\frac{1}{\sqrt{2}}$ E, or .707 times the impressed "delta" pressure.

The total energy stored in the condenser is constant at all times,

and is equal to $(3/2)CE^2$, where C is the capacity of one of the plates and E is the "delta" pressure impressed upon the cell.

The figures below are actual measurements made upon a three-phase aluminum condenser. The observed voltages are somewhat lower than the theoretical voltages.

THREE-PHASE CONDENSER PRESSURES.

Impressed pressure (delta voltage)	= 108 volts	Phase	1
	= 107 volts	"	2
	= 108 volts	"	3
Constant unidirectional pressure to neutral point	= 81	volts	
Theoretical value to neutral point	= 92.5	"	
Pressure with one of the electrodes disconnected	= 68	"	
Theoretical value	= 79	"	

ROTATING CHARGE.

An interesting point in connection with polyphase cells is that one may arrange the electrodes in a circle in the electrolyte and produce a rotating negative electrostatic charge in the electrolyte. In the single phase condenser it was pointed out previously that the negative charge may be considered to be sent back and forth from one electrode to the other.

In Figure 26 is shown a diagram of the pressures in a three-phase cell. The zero line represents the potential of the "neutral" point of the three-phase circuit. The sinusoidal curves represent the potentials of the three electrodes with respect to the neutral point. The potential of the electrolyte is represented by the straight line El-El.

The equivalent capacity for each phase of this three-phase condenser is one-half the capacity of one electrode.

SUMMARY.

This paper is a continuation of one read at the Fifth General Meeting of this Society. Hydraulic analogies of the aluminum condenser are shown. The resistance, dielectric strength and inductivity of the film are shown to be as high, or higher, than ordinary dielectrics. The resistance in one instance is shown to be about 10^{11} ohms per cubic centimeter. A value of about 5,000,-

000 volts per centimeter is obtained for the dielectric strength. A value of about 15 is obtained for the inductivity. The cell losses are analyzed graphically. The pressures between the cell terminals and between one of the electrodes and the electrolyte are

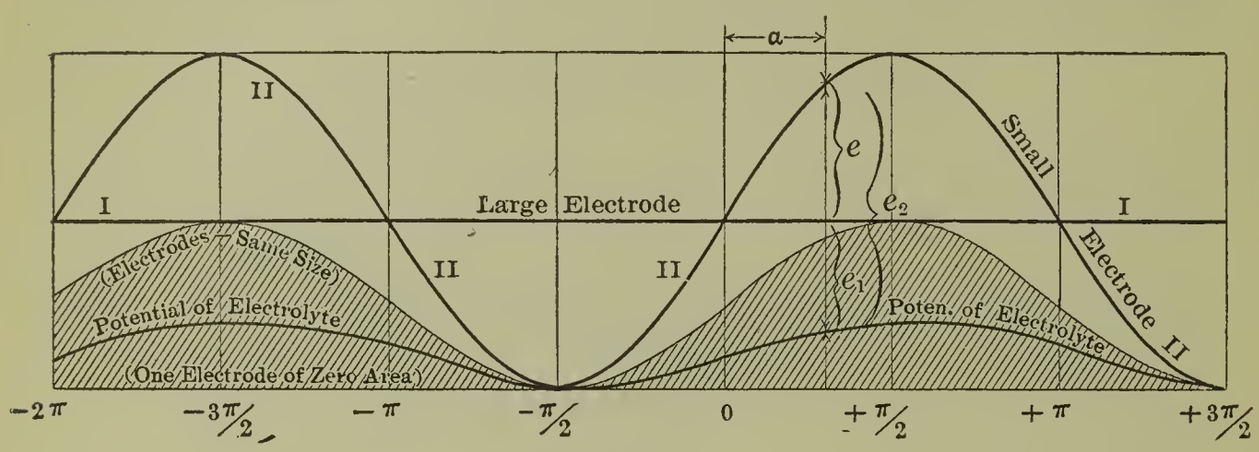


FIG. 27.

Showing the relation of the potentials of the electrodes where the electrodes are of different electrostatic capacities.

shown from 0 to 140 volts. It is pointed out that this cell affords a means of checking up A. C. and D. C. voltmeters. The unsymmetrical cell consisting of aluminum electrodes whose films

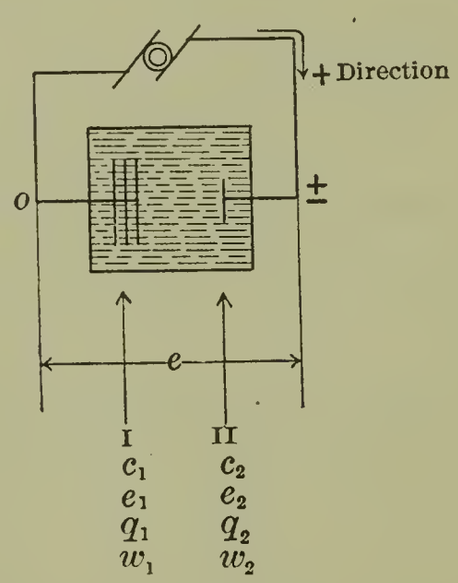


FIG. 28.

have different electrostatic capacities are discussed and analyzed graphically and mathematically. Oscillograph curves are shown of the different pressures. It is shown that the unidirectional pressures across each electrode may be considerably

greater than the impressed pressure. The behavior of the cell on alternating current circuit is, notwithstanding its peculiarities, similar to two tinfoil condensers in series. The "equivalent" capacity is $\frac{c_1 c_2}{c_1 + c_2}$ where c_1 and c_2 are the electrostatic capacities of the films on the two electrodes. Polyphase (2 and 3 phase) condensers are discussed. The three-phase condenser pressures are shown diagrammatically.

EQUATIONS OF THE ALUMINUM CONDENSER.

Explanation of the Symbols Used.

(a) I = Electrode No. 1 = Large Electrode in an Unsymmetrical Cell.

(b) II = Electrode No. 2 = Small Electrode in an Unsymmetrical Cell.

(c) C_1 and C_2 = Electrostatic Capacities of Electrodes I and II.

(d) C_0 = Electrostatic Capacity of Cell as a Condenser on A. C. Circuits.

(e) e_1 and e_2 = Instantaneous Pressures on Electrodes I and II.

(f) e = Instantaneous value of Impressed Pressure.
$(e = E_M \sin \alpha)$
$(e = e_2 - e_1.)$

(g) E_M = Maximum value of Impressed Pressure e.

(h) E = "Effective" value of Impressed Pressure; *i.e.*, $\sqrt{\text{average } e^2}$

(i) α = "Electrical" degrees of *Impressed Pressure Wave,* measured from the instant of zero value of pressure and when Electrode II is becoming Positive to Electrode I.

(j) q_1 and q_2 = Coulomb Charges on Electrodes I and II. (Instantaneous values.)

(k) Q_M = Maximum Coulomb Charge in cell = Constant at all times.
$(Q_M = C_1 E_M.)$

(l) w_1 and w_2 = Energy Charges on Electrodes I and II. (Instantaneous values.)

(m) $w_3 = w_1 + w_2$ = Instantaneous value of whole energy charge in cell.

The Fundamental Equations 1 to 4

For the purpose of comparison, the equations of two tinfoil condensers (in series) are given in the column to the right.

Aluminum Condenser	*Two Tinfoil Condensers*
(1) $e = E_M \sin\alpha = e_2 - e_1$	$e = E_M \sin\alpha = e_1 + e_2$
(2) (a) $Q_M = C_1 E_M = q_1 + q_2$ (b) $q_2 = C_1 E_M - q_1$	$q_1 = q_2$
(3) (a) $e_1 = q_1/C_1$ (b) $e_2 = q_2/C_2$	(a) $e_1 = q_1/C_1$ (b) $e_2 = q_2/C_2$
(4) (a) $w_1 = \frac{C_1 e_1^2}{2}$ (b) $w_2 = \frac{C_2 e_2^2}{2}$	(a) $w_1 = \frac{C_1 e_1^2}{2}$ (b) $w_2 = \frac{C_2 e_2^2}{2}$

Derived Equations (Instantaneous Values)

Aluminum Condenser	*Two Tinfoil Condensers*
(5) From (1), (3b) & (2b) $E_M \sin\alpha = \frac{C_1}{C_2} E_M - \frac{C_1 + C_2}{C_1 C_2} q_1$	$E_M \sin\alpha = \frac{C_1 + C_2}{C_1 C_2} q_1.$
(6) From (5) $q_1 = \frac{C_1 E_M}{C_1 + C_2} C_1 - \frac{C_1 C_2}{C_1 + C_2} E_M \sin\alpha$	$q_1 = \frac{C_1 C_2}{C_1 + C_2} E_M \sin\alpha$
(7) From (2b) and (6) $q_2 = \frac{C_1 E_M}{C_1 + C_2} C_2 + \frac{C_1 C_2}{C_1 + C_2} E_M \sin\alpha$	$q_2 = q_1 = \frac{C_1 C_2}{C_1 + C_2} E_M \sin\alpha$
(8) From (3a) and (6) $e_1 = \frac{C_1 E_M}{C_1 + C_2} - \frac{C_2}{C_1 + C_2} E_M \sin\alpha$	$e_1 = \frac{C_2}{C_1 + C_2} E_M \sin\alpha$
(9) From (1) and (8) or (7) and (3b) $e_2 = \frac{C_1 E_M}{C_1 + C_2} + \frac{C_1}{C_1 + C_2} E_M \sin\alpha$	$e_2 = \frac{C_1}{C_1 + C_2} E_M \sin\alpha$

(10) From (4a) and (8) * $w_1 = \frac{C_1 . C_1^2 E_M^2}{(C_1+C_2)^2 \times 2} - \frac{2 C_1^2 C_2 E_M^2 \sin \alpha}{(C_1+C_2)^2 \times 2} + \frac{C_1 C_2^2 E_M^2 \sin^2 \alpha}{(C_1+C_2)^2 \times 2}$	$w_1 = \frac{C_1 C_2^2 E_M^2 \sin^2 \alpha}{(C_1+C_2)^2 \times 2}$
(11) From (4b) and (9) ** $w_2 = \frac{C_2 . C_1^2 E_M^2}{(C_1+C_2)^2 \times 2} + \frac{2 C_1^2 C_2 E_M^2 \sin \alpha}{(C_1+C_2)^2 \times 2} + \frac{C_1^2 C_2 E_M^2 \sin^2 \alpha}{(C_1+C_2)^2 \times 2}$	$w_2 = \frac{C_1 C_2^2 E_M^2 \sin^2 \alpha}{(C_1+C_2)^2 \times 2}$
(12) From (10) and (11) *** $w_3 = w_1 + w_2 = \frac{C_1^2 E_M^2}{(C_1+C_2) \times 2} + \frac{C_1 C_2 . E_M^2 \sin^2 \alpha}{(C_1+C_2) \times 2}$	$w_3 = \frac{C_1 C_2 . E_M^2 \sin^2 \alpha}{C_1+C_2 \times 2}$

* Simplified $w_1 = \left\{ \frac{C_1 E_M^2}{2} \left(\frac{C_1 - C_2 \sin \alpha}{C_1 + C_2} \right)^2 \right\}$

** Simplified $w_2 = \left\{ \frac{C_2 C_1^2 E_M^2}{2} \left(\frac{1 + \sin \alpha}{C_1 + C_2} \right)^2 \right\}$

*** Simplified $w_3 = \left\{ \frac{C_1 E_M^2}{2} \left(\frac{C_1 + C_2 \sin \alpha}{C_1 + C_2} \right) \right\}$

Derived Equations (Integrated Values)

Since e_1 and e_2 are unidirectional pulsating pressures, their integrated values must balance each other during each cycle of the alternating pressure impressed upon the cell, *i. e.*, E′ average = E″ average.

(13a) $E'_{\text{average}} = \int_{-\pi/2}^{+3\pi/2} \frac{e_1 \, d\alpha}{2\pi}$ (13b) $E''_{\text{average}} = \int_{-\pi/2}^{+3\pi/2} \frac{e_2 \, d\alpha}{2\pi}$

where E'_{average} and E''_{average} are the average values of the unidirectional pressures on Electrodes I and II.

---

(14) From (8) and (13)

$$E'_{\text{average}} = E''_{\text{average}} = \int_{-\pi/2}^{+3\pi/2} \frac{E_M}{2\pi(C_1+C_2)} (C_1 - C_2 \sin \alpha)\, d\alpha$$

$$= \frac{C_1}{C_1+C_2} E_M \left(= \frac{C_1}{C_1+C_2} \sqrt{2}\, E \right)$$

---

(15) The "effective" * pressures on the films I and II are :

(a) $E'_{\text{effective}} = \sqrt{\frac{1}{2\pi} \int_{-\pi/2}^{+3\pi/2} e_1^2\, d\alpha}$

(b) $E''_{\text{effective}} = \sqrt{\frac{1}{2\pi} \int_{-\pi/2}^{+3\pi/2} e_2^2\, d\alpha}$.

When $E'_{\text{effective}}$ & $E''_{\text{effective}}$ are the "effective" values of the unidirectional pulsating pressures on Electrodes I and II.

---

(16) From (15a) and (8)

$$E'_{\text{effective}} = \frac{E_M \sqrt{2C_1^2 + C_1^2}}{\sqrt{2}\,(C_1+C_2)} \left(= \frac{E}{C_1+C_2} \sqrt{2C_1^2 + C_2^2} \right)$$

---

(17) From (15b) and (9)

$$E''_{\text{effective}} = \frac{C_1 E_M \sqrt{3}}{C_1 \times C_2 \sqrt{2}} \left(= \frac{E\, C_1 \sqrt{3}}{(C_1+C_2)} \right)$$

---

* "Effective" $= \sqrt{\text{average } e_1^2}$ or $\sqrt{\text{average } e_2^2}$

The Equivalent Capacity of the Condenser (C_0)

This may be obtained from the maximum and minimum values of the energy stored up in the cell. It will be readily seen from the simplified form of equation (12) that the maximum value occurs when $\sin \alpha = 1$, *i.e.*, at $\pi/2$; $3\pi/2$; $5\pi/2$, etc. The minimum value occurs at 0; π; 2π, etc.

$$(18)\quad (a)\ w_{\text{maximum}} = \frac{C_1 E_M^2}{2}$$

$$(b)\ w_{\text{minimum}} = \frac{C_1 E_M^2}{2} \frac{C_1}{C_1 + C_2}$$

$$(c)\ w_{\text{max.}} - w_{\text{min.}} \frac{C_1 E_M^2}{2}\left(1 - \frac{C_1}{C_1 + C_2}\right) = \frac{C_1 C_2}{C_1 + C_2} \frac{E_M^2}{2}$$

The equivalent capacity (C_0) of the cell is thus

$$(19)\quad C_0 = \frac{C_1 C_2}{C_1 + C_2}$$

Pittsburg, Pa., April, 1905.

DISCUSSION.

(*Communicated in advance of the meeting by Mr. W. R. Mott*).

Mr. C. I. Zimmerman's second paper on "The Aluminum Electrolytic Condenser" excels his first paper, which the Russians and French found well worth translation. Mr. Zimmerman has added to our knowledge of the aluminum electrolytic condenser by a scientific, mathematical discussion of its behavior under a variety of conditions. This discussion is well supported by some quite original experiments, and the numerical data is obtained with known current wave forms, and the best of celebrated electrical measuring instruments.

Mr. Zimmerman's two papers leave almost nothing to be done in the way of further analysis of the aluminum electrolytic condenser. But there are some details on the exact value of the electrical constants of the film that need further investigation.

The calculation of the absolute thickness of the film is somewhat difficult from an optical standpoint, because of the *unknown refractive index,* because of the *unknown structure* of the film, and finally because of the difficulty of exactly defining all the conditions of formation of the film.

Again, we have no data on the dielectric constant as obtained with films formed in different electrolytes.

However, Mr. Zimmerman has advanced our knowledge by finding the specific inductive capacity for a certain film to be 14.6.

A paper read at the Seventh General Meeting of the American Electrochemical Society, held at Boston, Mass., April 27, 1905. President Carhart in the chair.

A LOW VOLTAGE STANDARD CELL.

By Geo. A. Hulett.

W. Jaeger (Wied. Ann. 65, 106, 1898) and H. C. Bijl (Zeitsch. f. Phys. Chem. 41, 662, 1903), in studying the electromotive force of cadmium amalgams, have found that, at ordinary temperatures, all amalgams between 5 and 14 per cent. of cadmium have the same electromotive force (measured against any constant electrode). From Jaeger's work it is to be concluded that we may increase the per cent. of cadmium from 5 to 14 without varying the electromotive force by $\pm$ 0.000001 V.

Further, it is known that amalgams of cadmium, between these percentages, are made up of a solid and liquid phase, and from many analyses, Kerp and Böttger (Zeitsch. Anorg. Ch. 21, 1) have concluded that the solid is Cd_2Hg_7. On the other hand Bijl (l.c.) gives evidence to show that the solid phase is a mixed crystal. At 25° the mixed crystal appears when 5.3 per cent. of cadmium is present, and from this point to 15 per cent. of cadmium, the composition and electromotive force of the mixed crystal remains constant.

At 50° the range is from 10.3 to 18 per cent. of cadmium. These facts permit of the construction of a very simple low voltage cell represented by the following scheme:

Cadmium/Cadmium Sulphate/Cadmium Amalgam
5-13 %

Observations began in May, 1904, on this combination indicate that its electromotive force remains very constant, while cells set up at different times and with materials from different sources agree remarkably well, considering that one electrode is a metal in the solid state. It is the general experience that it is exceedingly difficult to get two electrodes of the same metal to agree, but the work on this cell indicates that this is not true of electrolytically deposited cadmium.

The only materials needed are cadmium sulphate and cadmium amalgam, for the cadmium electrode is deposited electrolytically after the cell has been set up. This permits of making the cell very small and much like a thermometer.

The glass part (Fig. 1) is a thin walled tube some 8-10 mm. in diameter, closed at one end and provided with a platinum wire (a), two or three centimeters above the closed end is a platinum spiral (b), with its end fused through the side of the tube (the wires are thoroughly cleaned with aqua regia before filling the cell).

In filling, the spiral is pressed to one side and some 0.5 cc. of 13 per cent. cadmium amalgam is brought into the lower

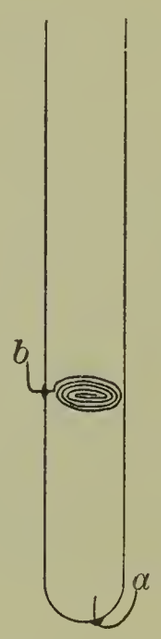


FIG. 1.

part and melted (carefully avoid bringing the amalgam in contact with the platinum spiral). Next the cell is filled to the spiral with $CdSO_4 \frac{8}{3}H_2O$ crystals. The spiral is pressed down on these crystals and more put on top, and then filled to above the crystals with cadmium sulphate solution or (since the electromotive force is the same whether the crystals are absent or present—one may merely fill to above the spiral with a cadmium sulphate solution). The part of the tube some 2 cm. above the solution is softened in a little blast flame drawn out and sealed off. Insulated copper wires are soldered to the platinum wires and the cell is placed in a long thin walled test tube 30 cm. long by 1.2 cm. diameter. The cell is covered with insulating oil, and the test tube case is closed

with a cork, which also holds the leads in place (Fig. 2). It only remains now to form the cadmium electrode, and this is done by a current of from .0005 and .002 amperes passing from the amalgam and depositing cadmium on the platinum spiral. It is necessary to deposit at least 20 milligrammes, for with less amounts I have lately obtained very variable results, a current of

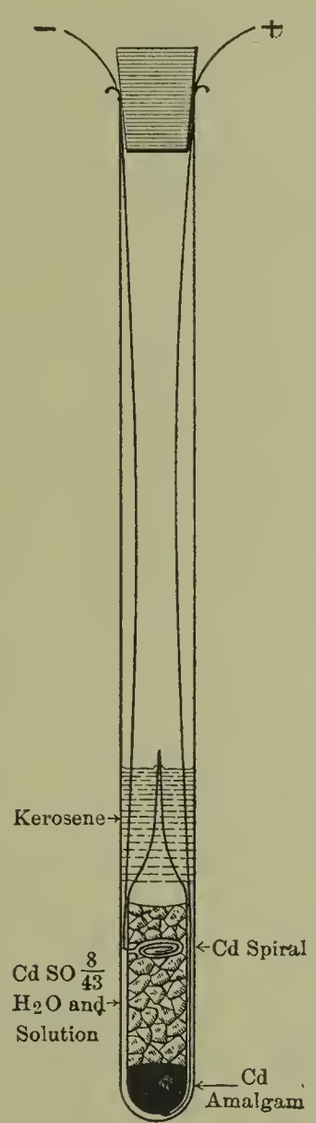


FIG. 2.

0.001A deposits about 0.002 gm. (2 milligrams) per hour, and most of my cells have been treated with such a current. The deposit is generally beautifully crystalline and compact, especially if the solid $CdSO_4\frac{8}{3}H_2O$ is in the immediate vicinity of the spiral, and the wires have been previously etched with aqua regia. But even a gray, spongy deposit in a dilute solution gives a value in close agreement with the others.

The electromotive force of this combination is 0.05175 international volts* at 20° C. The temperature coefficient is negative (— 0.000244) per degree, and practically linear. The temperature coefficient is higher than could be wished, but the cell, in the above form, takes up its true value in a remarkably short time, when brought from one bath to another, generally in less than 15 minutes. If placed in a bucket of water the cell follows any ordinary temperature change as readily as a mercury thermometer, so that a constant temperature bath is not required.

Only a little attention seems to have been given to this combination. Jaeger (Wied. Ann. 65, 107) notes that these constant electromotive force amalgams (5 to 14 per cent.) have an electromotive force 0.051 V below that of pure cadmium. Cohen (Zeitsch. für Phys. Chem. 34, 617) has studied the combination $Cd/CdSO_4/Cd$ amalgam 14.3 per cent. to get its value and temperature coefficient as a basis for calculating the heat of solution of cadmium in cadmium amalgam. His amalgam is just at the upper limit of the constant electromotive force amalgams and his value, .0513V at 20°, and his temperature coefficient are both lower than my value. Richards and Lewis (Zeitsch. Phys. Chem. 34, 1) have studied the combination with amalgams of about 1 per cent. cadmium, but no particular attention seems to have been given to the combinations with an amalgam well within the 5-14 per cent. range, and this work was taken up primarily as part of an analysis of the temperature coefficient of the cadmium standard cell. May 13, 1904, three cells were constructed very nearly as described above, excepting that about 100 mg. of Cd was deposited at the spiral and the amalgam was originally of such a strength that after the cadmium was deposited at the spiral the amalgam was left 12½ per cent. In the other cells 12½ per cent amalgam was used, and the cadmium decreased by the amount deposited on the spiral.

Table I gives an idea of the behavior of these cells, giving the date and temperature of the cells at the time of measurement, and it might be added that they were kept at 25.0° except during the days indicated and during the summer vacation. The table does

* I have a large number of Clark and Cadmium cells from the previous work on standard cells, and the above value is based on Clark 15° = 1.4340 V, and the $\frac{\text{Clark 15}}{\text{Cadmium 20}} = 1.406701$. The comparisons were made with a (Otto Wolf, Berlin) Teussner potentiometer reading direct to 0.00001 V.

Table I.

Number of Cell	Date of Construction	Electrolyte	Cadmium Deposited as Spiral	State of Deposited Cadmium	1904 May 16 25.0°	June 18 25.0°	July 27 25.0°	Aug. 4 25.0°	Nov. 21 25.0°	Nov. 24 25.0°	Nov. 29 25.0°	Dec. 2 25.0°	Dec. 15 25.0°	1905 Jan. 10 25.0°	Jan 17 18.05°	Jan 18 18 05°
	1904															
1	May 13	Molecular Solution, Cd SO_4	0.104 grs	Gray	.05390	.05061	.05073	.05060	.05055	.05055	.05053	.05053	.05053	.05056	.05223	.05223
2	May 13	Solid Cd $SO_4\frac{8}{3}$ H_2O Sat. Solution . .	0.104 "	Crystalline and Bright	.05074	.05055	.05056	.05055	.05055	.05056	.05053	.05053½	.05056	.05067	.05225	.05225
3	May 13	Solid Cd $SO_4\frac{8}{3}$ H_2O Sat. Solution	0.072 "	Crystalline and Bright	05050	.05053	.05056	.05057	.05050	.05050	.05050	.05050	.05052	.05055	.05225	05221
4	Nov. 17	Twis Molecular Solution . . .	0.020 "	Gray Spongy .	. . .	. . . .	. . . .	. . . .	.05101	.05070	.05056	.05056	.05056	.05055	.05226	.05226
5	Dec. 15	Solid and Sat. Solution	0.018 "	Crystalline and Bright	. . . .	. . . .	. . . .	. . . .	. . . .	. . . .	. . . .	. . . .	.05057	05055_5	.05226	.05226
6	Dec. 15	Solid and Sat. Solution	0 018 "	Crystalline and Bright	. . . .	. . . .	. . . .	. . .	. . . .	. . . .	. . . .	. . . .	.05057	$.05055_5$	$.05225_5$	.05225

Number of Cell	Date of Construction	Electrolyte	Cadmium Deposited as Spiral	State of Deposited Cadmium	1905 Jan. 19 0.0°	Jan. 21 0.0°	Jan. 23 18.02°	Jan. 24 25.0°	Feb. 9 25.0°	Feb. 14 25.00°	Mar. 17 25 00°	Mar. 25 25.00°	Mar. 26 30.00°	Mar. 29 25 00°
	1904													
1	May 13	Molecular Solution, Cd SO_4	0.104 grs.	Gray	.05667	.05669	.05225	.05055	.05054	.05054	$.05053_6$	$.05054_3$	$.04932_5$	$.05055_8$
2	May 13	Solid Cd $SO_4\frac{8}{3}$ H_2O Sat. Solution	0.104 "	Crystalline and Bright	.05669	.05673	.05227	.05057	.05056	.05056	.05055	05054_6	.04933	$.05055_5$
3	May 13	Solid Cd $SO_4\frac{8}{3}$ H_2O Sat. Solution	0.072 "	Crystalline and Bright	.05667	.05666	.05225	.05052	.05050	.05050	$.05054_8$	$.0\ 053_0$	$.04930_6$	$.050^{-}4_4$
4	Nov. 17	Twis Molecular Solution .	0.020 "	Gray Spongy	.05676	.05669	$.05225_5$	.05056	.05056	.05056	.05055	$.05054_8$	.04933	$.05055_8$
5	Dec. 15	Solid and Sat. Solution . .	0.018 "	Crystalline and Bright	.05676	$.05669_5$	.05226	$.05056_5$	.05056	05056	This cell was sent to Prof. Bolles Columbia School of Mines.			
6	Dec. 15	Solid and Sat. Solution . .	0 018 "	Crystalline and Bright	.05675	.05668	05225	.05055	.05055	.05051	.05054	.05054	04932	.05054

not include all the measurements made, but is intended to give an idea of the variations of these cells. A number of cells were made with addition of Cd $(OH)_2$ thinking this might make a more uniform cadmium deposit; also the air was completely removed from three before sealing, and in others the air was removed and the cell saturated with nitrogen and with hydrogen. All of these gave very variable results, but in each case only 10 milligrams of cadmium had been deposited on the spiral, and I have lately learned this is too little cadmium, since some cells set up as above described, excepting that only 10 mg. of cadmium was deposited on each spiral, showed the same irregularities and tendency to constantly decreasing electromotive force. These cells were recently all discharged and then reversing the current about 26 mg. of cadmium was deposited on each platinum spiral, and they seem to be all coming together nicely and to the value indicated by the old cells.

The electromotive force of these cells is high when the cadmium is freshly deposited, and the length of time required to reach the normal value seems to depend on the thickness of the deposit. Air free cells and those saturated with $Ca(OH)_2$ behave like the others and I have as yet no explanation of the high e. m. f. of newly constructed cells.

Cell No. 4 is remarkably constant; after reaching its normal value (two weeks after it was constructed) it has not varied more than $\pm$ 0.00001 V. There was no solid $CdSO_4$ H_2O in this cell, but the electrolyte was two molecules of cadmium sulphate to the liter. It is hoped that a further study of these cells will make them reproducible to the variations shown by Cell 4. The simplicity of the combination permits of a form that is exceedingly convenient and far superior to the ordinary form. The construction of the cell is a comparatively simple operation, while the materials are well defined substances and easily obtainable.

The small electromotive force is an objection for a primary standard, but there is a very considerable amount of work done in which small electromotive forces are to be accurately measured—for example, temperature measurements with a thermo couple. For such work one can easily construct a potentiometer from materials that are generally at hand. A slidwire bridge of some 20 ohms resistance, a regulating resistance, storage bat-

tery, and a galvanometer that will do for a zero instrument. The battery circuit is closed through the bridge and regulating resistance. The galvanometer and standard cell are joined in series to the positive end of bridge and the slide contact. The regulating resistance of the battery circuit is varied until say, there is balance at 517 mm. of bridge (cell at 20°), and then 1 mm. = 0.0001 V and the whole bridge = 0.100 V.

The fact that the electromotive force and temperature coefficient of these cells is not only independent of the concentration of the electrolyte but even of the presence or absence of the solid salt make them particularly interesting. A cell set up with cadmium chloride seems to be coming to about the same value. It seems that the electromotive force is independent of the electrolyte, but depends only on the electrodes. The cell is evidently strictly reversible at both electrodes, but it does polarize, and is only to be used in the Poggendorf compensation method. The internal resistance is very small. In ordinary Clark or cadmium cells the internal resistance is 600 and 1,000 ohms.

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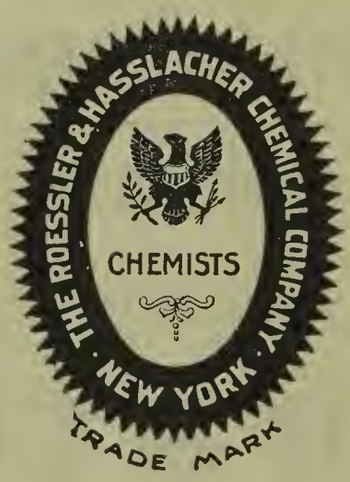

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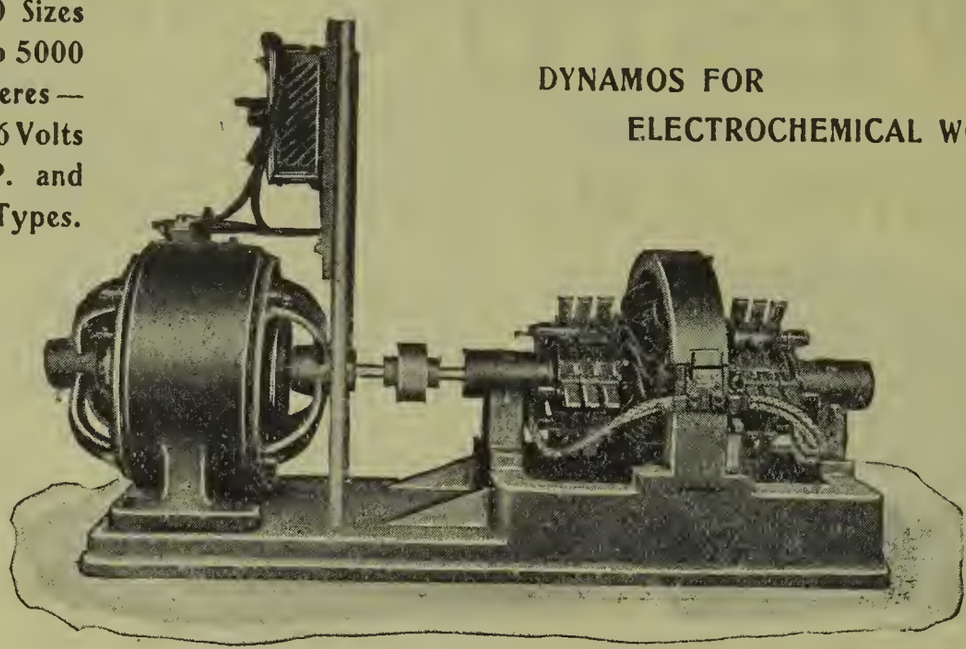

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